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THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS,
ERNEST MERRITT, and FREDERICK BEDELL

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JULY, 1911

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THE

PHYSICAL REVIEW.

THE NATURE OF LIGHT ACTION IN SELENIUM.

By F. C. Brown.

IN a paper by Brown and Stebbins[1] it was shown that the light-sensitiveness of a certain selenium cell was a function of its resistance whether that resistance was conditioned by temperature, pressure, light or other agencies. This conclusion, together with the results of recent investigations, has led me to formulate an hypothesis for explaining the changes in the electrical conductivity occurring in light-sensitive selenium. The statement and the discussion of this hypothesis together with the results of investigations pertinent to this hypothesis will form the material of this paper. As the amount of data that must be correlated is quite large indeed, particular attention will be given only to the various effects produced by light.

The hypothesis is that all light-positive and light-negative varieties[2] of selenium consist of various mixtures of three kinds of selenium which we will call A, B and C, and that under the action of light A is changed into B and B is changed into C, according to the reaction,

$$A \rightleftarrows B \rightleftarrows C$$

and that the changes in both directions are proportional at all times to the amounts of the changing material. The principal argument that is offered for proposing such an explanation is that it seems to be consistent with the experimental facts under a variety of conditions, and that as is generally recognized previous theories do not explain many of the recently observed phenomena.

That the effect of illumination on certain varieties of light-positive selenium is to produce a genuine change in the selenium itself has not

[1] Phys. Rev., 26, p. 273, 1908.

[2] For the meaning of this terminology see Phys. Rev., XXXII., p. 237, 1911.

been questioned since Pfund[1] and Berndt[2] showed that selenium cells made by using selenium of the highest purity and carbon electrodes were sensitive to light. By studying the conductivity at different temperatures Marc[3] concluded that certain varieties of selenium consist of two allotropes A and B in equilibrium. Montén[4] by observing the resistance in the dark at pressures between 0 and 3,000 atmospheres concluded that the selenium cells that he used consisted of at least two allotropes A and B in equilibrium under the given pressures.

More recently Kruyt[5] has made density measurements that indicate that in light-sensitive selenium there are two components that are in equilibrium according to the reaction $A \rightleftarrows B$.

This paper will not attempt to define the three components whose existence is supposed nor will it consider the particular reasons why the components have different rates of change under the same external conditions. But since Biltz and Preuneur[6] have found three components in sulphur changing under the influence of pressure and temperature according to the reaction

$$S_8 \rightleftarrows S_4 \rightleftarrows S_2$$

it would not be surprising to find later that the three components of light-sensitive selenium may be identified and studied as separate allotropic forms.

THEORY.

In order to obtain conditions which are easily subject to theoretical treatment we will suppose that the sensitive layer of selenium may be so thin that the impinging light may be of practically uniform intensity throughout the layer, and that temperature, pressure and all other conditions except that of illumination that affect the conductivity remain constant; further suppose that the conductivity of the A kind is zero, while that of the B kind approaches that of the metals and that the conductivity of the C kind is so much smaller than that of the B kind that it may be neglected. Part of the experimental evidence in favor of neglecting the conductivity of the C kind will be brought out in this paper but the most direct evidence will be presented in a later paper concerning the recovery of selenium. Let α_1 and β_1 be the respective rates of change of A into B and B into C for a given set of conditions and α_2 and β_2 the

[1] Phil. Mag., 7, p. 26, 1904.

[2] Phys. Zeit., 5, p. 121, 1904.

[3] Zeit. anorg. Chem., 48, p. 5, 1906.

[4] Archiv. för Matematik, Astronomi och Fysik, 4, p. 1, 1908, also dissertation on "The Influence of Pressure on the Electrical Resistance of Selenium and Silver Sulphide."

[5] Zeit. für anorg. Chemie, 64, p. 305.

[6] Zeit. Phys. Chem., 39, p. 323.

corresponding reverse changes of C into B and of B into A. Let A_0, B_0 and C_0 represent the initial amounts of the respective kinds before illumination. By illumination the constants α_1 and β_1 increase in value and are probably accompanied by small changes in α_2 and β_2, so that after a time t_1, the respective amounts of the three kinds are A_1, B_1 and C_1. Nothing will be said concerning the homogeneity and uniformity further than that the way in which the three components are mixed shall not to any great extent affect the following expression for the conductivity,

$$i = K_1 B. \tag{1}$$

Then the changes take place in accordance with the following equations:

$$dA/dt = \alpha_2 B - \alpha_1 A, \tag{2}$$

$$dB/dt = \alpha_1 A - \alpha_2 B + \beta_2 C - \beta_1 B, \tag{3}$$

$$dC/dt = \beta_1 B - \beta_2 C, \tag{4}$$

$$A + B + C = K, \tag{5}$$

$$dA/dt + dB/dt + dC/dt = 0. \tag{6}$$

From these equations we obtain the differential equation,

$$[\ddot{B}] + (\mu + \alpha_1)[\dot{B}] + (\alpha_1\mu - \alpha_2\lambda)B - \beta_2\alpha_1 K = 0, \tag{7}$$

where

$$(\alpha_1 - \beta_1) = \lambda,$$

$$\alpha_2 + \beta_2 + \beta_1 = \mu.$$

This equation is of the form,

$$[\ddot{B}] + M[\dot{B}] + NB - L = 0.$$

The solution of the equation is

$$B = L/N + c_1 e^{+m_1 t} + c_2 e^{m_2 t}, \tag{8}$$

and

$$C = \frac{L\beta_1}{N\beta_2} + \frac{\beta_1 c_1 e^{m_1 t}}{\beta_2 + m_1} + \frac{\beta_1}{\beta_2 + m_2} c_2 e^{m_2 t}, \tag{9}$$

where

$$L = \alpha_1\beta_2 K, \tag{10}$$

$$N = \alpha_1\beta_1 + \alpha_1\beta_2 + \alpha_2\beta_2, \tag{11}$$

$$m_1 m_2 = \alpha_1\beta_1 + \alpha_1\beta_2 + \alpha_2\beta_2, \tag{12}$$

$$m_1 + m_2 = -(\alpha_1 + \alpha_2 + \beta_1 + \beta_2), \tag{13}$$

$$B_0 = L/N + c_1 + c_2, \tag{14}$$

$$C_0 = L/N \times \beta_1/\beta_2, \tag{15}$$

for equilibrium in the light,

$$B_1 = \frac{L}{N} = \frac{(\alpha_1\beta_2)K}{\alpha_1\beta_1 + \alpha_1\beta_2 + \alpha_2\beta_2}, \tag{16}$$

$$C_1 = \frac{L}{N} \times \frac{\beta_1}{\beta_2} + \frac{\beta_1}{\beta_2 + m_1} c_1 + \frac{\beta_1 c_2}{\beta_2 + m_2}, \tag{17}$$

$$\frac{\alpha_2}{\alpha_1} B_1 + B_1 + \frac{\beta_1}{\beta_2} B_1 = K, \tag{18}$$

and the value of the constants in equation (8) are

$$c_1 = \left[\frac{C_0}{\beta_1} + \left(\frac{L}{N} - B_0\right) \frac{1}{\beta_2 + m_2} - \frac{L}{N\beta_2}\right] \left[\frac{(\beta_2 + m_2)(\beta_2 + m_1)}{m_2 - m_1}\right], \tag{19}$$

$$c_2 = \left[\frac{C_0}{\beta_1} + \left(\frac{L}{N} - B_0\right) \frac{1}{\beta_2 + m_1} - \frac{L}{N\beta_2}\right] \left[\frac{(\beta_2 + m_2)(\beta_2 + m_1)}{m_1 - m_2}\right]. \tag{20}$$

Since the conductivity depends only on the amount of the B kind present, our problem is to determine how the amount of the B kind should

TABLE I.

Case.		1	2	3	4	5
After illumination	a_1	.13	.13	.03	10	10
	a_2	10.	10.	.40	.13	.13
	β_1	2.66	2.66	.40	2.66	2.66
	β_2	.05	.05	.3	.05	.05
	m_1	−10.39	−10.39	−.7	− 2.65	− 2.65
	m_2	− .058	− .058	−.2	−10.19	−10.19
	A_0	14,890.	121,000.	290.	12,880.	2,220.
	B_0	1.0	1.0	10.	10,000.	10.000.
	C_0	1.0	10,000.	10.	85,120.	95,760.
	A_1	9,320.	77,000.	265.	30.	30.
	B_1	120.	1,000.	20.	2,000.	2,000.
	C_1	6,360.	53,000.	25.	106,000.	106,000.
	K	15,900.	131,000.	310.	108,000.	108,000.
	L/N	120.	1,000.	20.	2,000.	2,000.
Per cent. A_0		90.	92.	90.	12.	2.
Per cent. B_0		.06	.008	3.2	9.0	9.0
Per cent. C_0		10.	8.	7.	79.	89.0
Before exposure	a_1/a_2	$.67\times10^{-4}$	8×10^{-5}	.035	.8	5.0
	β_1/β_2	1.0	10^3	1.0	8.5	9.5
After exposure	a_1/a_2	.013	.013	.075	77.	77.
	β_1/β_2	50.	50.	1.2	53.	53.

vary with the time of illumination, as specified in equation (8), when different initial conditions are considered. To do this we must first determine the constants m_1 and m_2 and c_1, c_2 and L/N. These constants depend on the rates of change and the initial amounts of the A, B

and C components. The rates of change must be positive quantities under all conditions. In accordance with equations (12) and (13) this obviously requires that m_1 and m_2 shall always be of negative sign. Also the amount of the three components A, B and C must necessarily be positive quantities, and it seems reasonable to expect that the ratios α_1/α_2 and β_1/β_2 should always be increased by the action of light. This last presumption would further require that during illumination the amount of the C kind must always be increased and that at the same time the A kind must be decreasing. The B kind may obviously either increase or decrease depending upon the relative amounts of change in the A and C kinds. These are all the conditions that it seems wise to impose at present. Further experimentation may show that not only do the rates of change vary according to simple laws with changes in the intensity but that the ratios of the rates also vary according to correspondingly simple laws.

By a method of approximations and guesses I have found specimen arbitrary values for the rates of change, which when taken with appropriate values of the other constants will establish the characteristic ways in which the conductivity, i, will vary with the time of exposure to light. All the constants must be in harmony with the twenty equations given and also must satisfy the other necessary conditions. The equation as obtained from (1) and (8) shows the relation between the conductivity and the time of exposure to be

$$i = K_1(L/N + c_1e^{m_1t} + c_2e^{m_2t}). \quad (21)$$

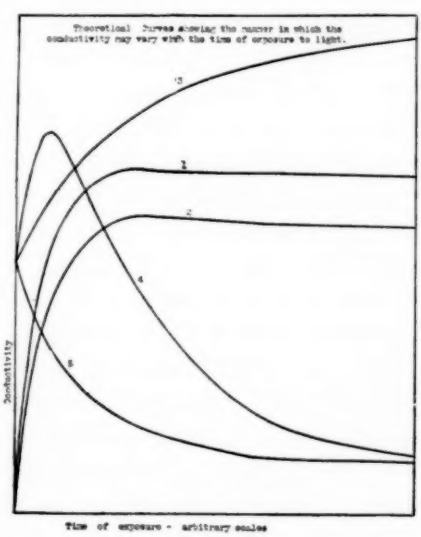

Fig. 1.

Certain values of the constants and other information is given in the accompanying Table I. This table furnishes the values for the constants in the above equation, the graphs of which are shown in Fig. 1. The equations of the curves are as follows;

curve 1, $B = 120 - 138e^{-10.39t} + 19e^{-.058t}$,
curve 2, $B = 1000 - 1160e^{-10.39t} + 160e^{-.058t}$,
curve 3, $B = 20 - 4.872e^{-.7t} - 5.12e^{-.2t}$,
curve 4, $B = 2000 - 3250e^{-10.59t} + 11250e^{-2.65t}$,
curve 5, $B = 2000 + 5670e^{-2.65} + 2340e^{-10.59t}$.

The main points that are essential to the theory may be understood most easily by studying the curves. In (1) and (2) the initial conductivity is very small and it rises rapidly to a maximum and then falls off slowly to a constant limiting value. The equilibrium value of the conductivity in the light to that in the dark is of the ratio 1,000 to 1. Curve (3) shows the conductivity in the dark to be greater than that shown in (1) and (2). The increase of conductivity due to illumination is always positive. It increases most rapidly at first. In the fourth case the conductivity rises rapidly by illumination to a maximum, that is, relatively to the initial conductivity not very large and then falls off quite rapidly to a value which may be even less than the initial conductivity. Curve (4) shows the manner of variation although it does not show the fact that the initial conductivity is much larger than prevails in the first three cases.

In what is called case 5 the conductivity begins to decrease at once when the light acts on the selenium and it falls rapidly compared to the rate of decrease in the other four cases noted.

Considerable importance is attached to the fact that the decrease of resistance becomes more and more rapid as the conditions change from those required in case 1 on down to those required by case 5, and that in all the cases except No. 5 there are changes in the conductivity in both directions shown in an unmistakable manner; also to the fact that as we shift from cases 1 to 5 the initial or dark conductivity increases.

Case 2 is regarded as a highly improbable one in that the rates of change between B and C compared to the reverse changes between C and B are greater before illumination than afterwards.

The theory proposed is simple and attractive in so much as it rather implies that all the agencies that affect the conductivity of selenium produce the same kind of a change in the selenium, namely a variation in the rates of interchange. Or stated in other words the selenium is in equilibrium under a variety of conditions. Each agency merely acts in a way to alter the equilibrium by changing the rates. Whether or not every agency changes the rates in accordance with the same laws after the units have been properly adjusted is a matter that will have to be determined by experiment. Any variety of selenium which shows a marked increase of conductivity at first and then is followed by a decrease when acted on by light should in all probability show the same two changes when acted on by other agencies, but this conclusion is clearly not required. For example, a Giltay or a high sensibility selenium cell which by illumination rises to a maximum conductivity, say 100 times as great haste conductivity in the dark, and then falls to only 30 times the

dark conductivity, might reasonably be expected to rise to the same maximum and then to fall to the same limiting value 30 to 1, if there were a sudden application of mechanical pressure of the right amount. The same argument would apply to the agencies of temperature and differences of electric potential.

A mechanical interpretation of the theory may be proposed as follows: The A, B and C varieties because of their rates of interchange are in equilibrium. When the selenium is illuminated new rates are established and consequently new equilibrium values for the amounts of the A, B and C kinds. We may regard the selenium as distorted from its equilibrium condition, and the study of the change of conductivity as merely a study of one of the processes taking place while the new equilibrium is being established. In fact experiment shows that it is possible to distort the selenium system, if it may be called such, so that the amount of any kind may be either greater or less than is required for equilibrium. So far as the B kind is concerned the distortion may be either positive or negative in at least one variety of selenium, while the condition of light or darkness is changing in only one direction. Or suppose any variety of selenium in equilibrium in the diffuse light of a room; the selenium may be distorted in one direction by imposing the condition of darkness. It may be distorted in the opposite direction by imposing the condition of intense illumination. By increasing the intensity of illumination the amount of the C kind increases and by decreasing the illumination the amount of the C kind decreases. The following argument will illustrate what general behavior is expected. Suppose a selenium cell in equilibrium in the dark in a condition which we will call ϕ. Next expose it to intense light and as a result of the existing distortion it changes according to certain laws toward a new equilibrium condition which we may call θ. The changes can be shown by curves. Finally remove the selenium to the dark and again due to the distorted condition of the selenium it will return to its former dark condition ϕ. The changes from θ to ϕ can also be represented on curves. The general movement of the change in the first case may be said to be in the positive direction and in the second case it may be said to be in the negative direction. The changes in the negative direction as shown by the second set of curves may be said to be the reciprocal of the changes in the positive direction and the time taken for the selenium to go from θ to ϕ should be of the same order of magnitude as the time required for the selenium to go from ϕ to θ. Where there is a rapid change and a slow change going in one direction there should in general be both the rapid and the slow changes in the reverse process.

In a recent paper[1] given before the American Physical Society was developed an equation for the conductivity on the assumption that the reverse changes α_2 and β_2 were at all times small compared to the direct changes, and that the conductivity of the C kind was one half as large as that of the B kind. It was stated that these assumptions were only tentative. As certain facts are brought out both by the agreement and by the disagreement of the experimental results with the equation developed,

$$i = k_1 \left\{ \frac{A_0 \alpha_1}{\alpha_1 - \beta_1} (e^{-\beta_1 t} - e^{-\alpha_1 t}) + B_0 e^{-\beta_1 t} \right\}$$

$$+ k_2 \left\{ \frac{A_0}{\alpha_1 - \beta_1} [\alpha(1 - e^{-\beta t} - \beta(1 - e^{-\alpha t})] + B_0(1 - e^{-\beta_1 t}) + C_0 \right\}$$

two families of curves taken from this equation are shown in Fig. 2 and Fig. 3. The theoretical objection that is urged against these

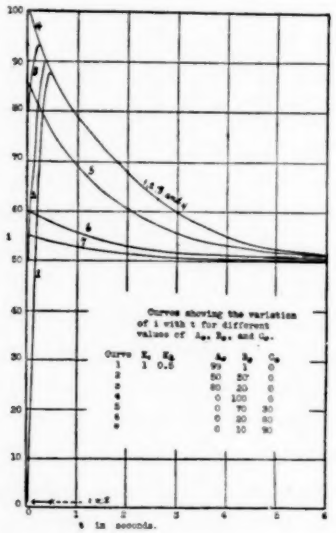

Fig. 2.

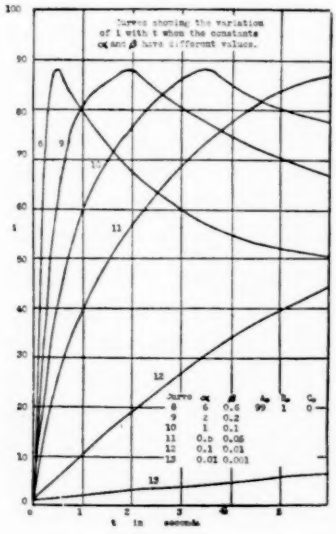

Fig. 3.

special assumptions is that there is no method of accounting for the initial amounts of the three kinds in the dark, and consequently no satisfactory way of explaining the recovery of the selenium after the light is removed. Wherein the experimental results show that the special assumptions are not warranted will be brought out in the discussion of the results.

[1] PHYS. REV., Vol. XXXII., p. 237, 1911.

General Considerations.

Some time ago I observed a striking relation between the resistance of selenium and its sensibility to light. In this instance, sensibility is used in the sense of the ratio of the conductivity in the light to the conductivity in the dark, when the selenium was exposed directly to sunlight or its equivalent for about 5 minutes. The relation observed was that the higher the resistance the greater was the sensibility or conversely the lower the resistance the less the sensibility and finally when the resistance became very low the sensibility became of the negative sign. The accompanying Table II. shows the observations that were made. However it must be remembered that the values represent only orders of magnitude. The specific resistance is not in all cases proportional to the measured resistance of the selenium. Further as the sensibility was measured without any intention of making such comparisons as here noted, the sensibility also is subject to a large error. Nevertheless the relation mentioned is very clearly shown.

Table II.

Kind of Selenium.	Resistance.	Sensibility.
High sensibility selenium cell,	10^9	200 to 1
Giltay selenium cell,	400,000	30 to 1
Ruhmer selenium cell,	90,000	10 to 1
Home made, 1904,	100,000	10 to 1
Home made, 1904	160,000	4 to 1
Home made, 1904,	30,000	2 to 1
Home made, 1904,	17,000	1.1 to 1
Home made, 1904,	12,000	1.0 to 1
Home made, 1904,	3,500	1.0 to 1
Light negative selenium,	400	−1.002 to 1
Light negative selenium,	20	−1.15 to 1
Light negative selenium,	1	−1.5 to 1

Since making these observations I have learned that Pochettino and Trabacchi[1] and also J. W. Giltay have made observations that show this same relation existing between resistance and sensibility. Giltay in one of his trade circulars on selenium cells, says that he makes high resistance selenium cells of high sensibility and low resistance selenium cells of low sensibility and adds that "low resistance and high sensibility simply do not go together."

As an example of diverse facts concerning selenium, which do not seem to any conclusion we may note the laws of change of conductivity with light intensity as given in Table III., where m represents the

[1]According to Ries in his book on Die Elektrischen Eigenschaften und die Bedeutung des Selens für die Electrotechnik.

change of conductivity, i represents the light intensity, R the resistance, and the other quantities constants.

TABLE III.

Law.	Authority.
$i = cm^2$	Rosse, Adams, Berndt.
$i = cm^3$	Hopius.
$i = m(m-a)b$	Athanasiadis.
$i = b^m - 1$	Hesehus.
$R_a/R_b = (b/a)^a$	Ruhmer.
$I = cm$	Stebbins.[1]

Without doubt all the variations in the results of the above investigators can be explained on the ground that the conditions were widely different in many cases. The varieties of selenium were not the same; the intensity ranged between different limits; and no doubt the time of exposure was different in each case. Other legitimate reasons might be sought for in the construction of the cell form and the thickness of the selenium on this form. The facts in this table are presented merely to demonstrate the futility of search for a simple universal law connecting the conductivity of a selenium cell and the intensity of illumination. It is obviously necessary to look to other relationships than the one mentioned if we wish to connect the facts by simple laws.

The properties of the known varieties of selenium are summed up in Table IV., so far as information has been obtained. The purpose here is to call attention in a more general way more particularly to the diverse properties of selenium.

TABLE IV.

Variety of Selenium.	Change of Conductivity by Light.	Conductivity in the Dark.	Direction of Change of Conductivity.			
			By Temperatures.	By Pressure.	By Electrical Diff. Potential.	By Moisture.
High sensibility cell	+ followed by −	10^{-9}	−	?	+	+
Giltay cell	+ followed by −	10^{-6}	+	+	+	?
Ruhmer cell	+	10^{-5}	+	+	+	+
Ries's "abnormal cell" . .	+ followed by −	?	?	?	?	+
Light-negative cell	−	10^{-2}	+	?	+or−	−

It is not certain how many of these diverse properties may be in part due to impurities in the selenium. Also we are very much in doubt as

[1] Proved by Stebbins for faint illumination by two independent methods in connection with his work on the Measurement of the Light of Stars by a Selenium Photometer, in Astro-Phys. Jour., 32, p. 185, 1910. However his results are not published.

to what is the depth of penetration of selenium by light. Before the proposed theory can be put to a rigid test it will be necessary to answer the last question but not the first. But this question cannot be answered at present. We may now proceed to call attention to experiments with the above varieties of selenium.

Experiments with Light-Positive Selenium.

In most of the experiments with light-positive selenium, a selenium cell designated Giltay No. 2, which was made by Giltay of Delft, Holland, was used. For somewhat more than a year previous to its use for the experiments described in this paper it has been left in paraffin oil in a glass tube of about 4.5 cm. diameter and 25 cm. length. With the exception of a space left for a window, the tube had been black enameled on the exterior surface. This tube was surrounded by a second similar tube. When the second tube was so turned that the two windows were together, the cell could be illuminated. The temperature of the oil in which the cell was placed was read from a thermometer projecting through a rubber cork down into the oil. In the dark at 25° C. the cell had a resistance of about 490,000 ohms.

Whenever changes in the conductivity were investigated that occurred during short intervals of time, a pendulum and a ballistic galvanometer were used in connection with a Wheatstone's bridge circuit. This method of measuring such changes of resistance is discussed elsewhere.[1] It will be sufficient to state here that the average conductivity of the selenium during any interval is a function of the deflection of the galvanometer, which function can be determined either by experiment or calculation. The method of illumination was to place a tungsten lamp in the same dark box in which the selenium cell was placed and to regulate the time of illumination by opening and closing keys controlling the current through the lamp. If the period of illumination desired was a fraction of a second, the keys were manipulated entirely by the pendulum which threw in the ballistic galvanometer. It was assumed that the light reached a constant value at once and no correction was made for the fact that the candle-power of a tungsten lamp decreases perceptibly after the current is turned on.

The change of conductivity varies with the time of illumination. In all high sensibility selenium cells the conductivity first rises rapidly to a maximum and then it falls off fairly rapidly at first and then more slowly. This is shown for the Giltay No. 2 in curve 14 of Fig. 4, where the cell was exposed to a 16-cp. lamp at about a distance of a meter.

[1] See paper by Brown and Clark, Phys. Rev., 1911.

The maximum conductivity is reached in about 50 sec. and is about seven times greater than the conductivity in the dark. In curve 15 is shown the variation of conductivity with time for a very intense illumination. The intensity was approximately that of a 32-cp. lamp at a distance of 7 cm. It will be noted that the maximum conductivity is reached in .35 sec.

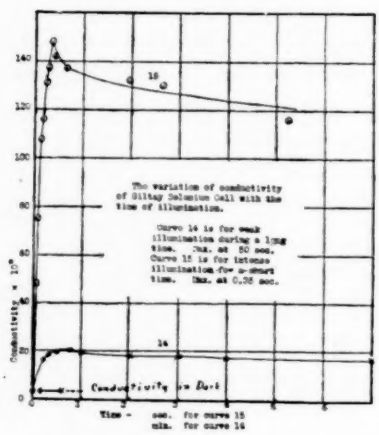

Fig. 4.

A fair sample of the observations taken to obtain the data for such a curve is given in the following Table V. The first key closes the storage battery circuit through a tungsten lamp. The second key throws the ballistic galvanometer in circuit and the third key again opens the galvanometer circuit.

There are three sources of error in obtaining these observations which for our present considerations are of minor importance. The first arises from the fact that the intensity of illumination of a tungsten lamp does not become constant at once when the current is turned on. The second error was in the current itself. The storage battery used did not

TABLE V.

Observations on the Change of Conductivity of Selenium Cell Giltay No. 2 with Time by Use of Pendulum and Ballistic Galvanometer.

Temp.	Resistance in Dark.	Distance Apart of Second and Third Keys.	Time of Exposure.	Mean Corrected Time.	Deflection.	Conductivity $\times 10^6$.
			0	0	0	2.7
28° C.	370,000	.1 sec.	0.1 sec.	0.050	28	48
		.05	0.1	0.075	35	75
		.05	0.15	0.125	41	107
		.05	0.2	0.175	45.5	116
		.05	0.25	0.225	50.8	131
		.05	0.30	0.275	52.5	137
		.05	0.35	0.325	56.5	148
		.05	0.40	0.375	52.5	137
		.05	0.40	0.375	53.1	141
		.05	0.65	0.625	52.4	137
		.05	2.65	2.62	48.9	130
		.05	2.0	1.97	48.1	129
		.05	5.25	5.22	45.0	115
		.05	9.4	9.4	41.	107

furnish an unvarying E.M.F. After a few seconds use there was observed several times a slight decrease in the current. If however the lamp was connected in the regular lighting circuit substantially the same results were obtained as when the storage battery was used. The third error arose from incomplete recovery between readings. Practically from 1 minute to 1 hour was considered sufficient time, the time depending upon the intensity and duration of exposure and the temperature. For reasons which will be given later, we shall see that the reaching of the initial dark resistance does not necessarily require that the equilibrium condition shall be reached for a particular temperature or light condition. But equilibrium does require a particular resistance, under given conditions.

The amount of the decrease of conductivity in the Giltay cell is by no means pictured in curve 15. Other sets of observations were made where the time of illumination extended over a period of 15 minutes, *i. e.*, about one hundred and fifty times as long as in the instance just discussed. A Siemens and Halske needle galvanometer was placed in series with the cell and the conductivity was determined directly from the readings. The intensity of illumination was approximately the same as that for the short exposure. The decrease of the conductivity was extremely large as will be readily seen by referring to curves 16 and 17 of Fig. 5. In these cases the maximum conductivity was probably reached in 0.4 sec. At the temperature of 17° C. the conductivity was of the order of one hundred times that of the conductivity in the dark and at 41° C., the maximum ratio of the two conductivities was about 30 to 1. It may be observed from the curves that these ratios decreased after 10 minute exposures to 60 to 1 and 12 to 1. These last ratios probably represent very nearly the condition of equilibrium with the given intensity of light compared with equilibrium in the dark for the two temperatures stated. It is significant however that the equilibrium is approached with equilibrium in the dark for the two temperatures decidedly more rapidly at the higher temperature. The first deflection of 40 recorded in curve 17 is no doubt somewhat too high, due to the inertia of the galvanometer needle system.

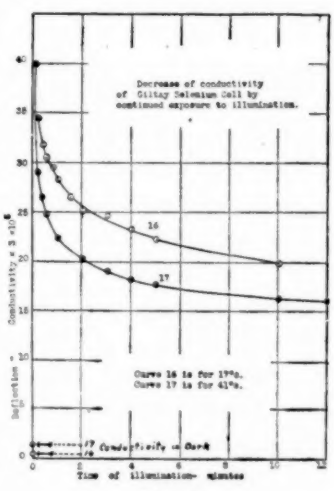

Fig. 5.

The remarkable decrease in the conductivity of the Giltay cell is just as remarkable as is the enormous increase at first. Certainly it is of just

as much importance theoretically. First of all it is quite necessary to know if this decrease in the conductivity represents a genuine change in the selenium or if it is a polarization phenomenon. This question is a particularly legitimate one in view of the fact that many selenium cells show extreme polarization under the action of light and the electric current. I wish to state at the outset that none of the phenomena I have observed recently in light-positive and light-negative selenium arise from polarization by the current. My reasons for making such deductions with regard to the Giltay cell are as follows:

(*a*) First the selenium cell was balanced in a Wheatstone's bridge circuit after being intensely illuminated for several minutes. Then the battery circuit was broken. There was not the slighest deflection of the galvanometer by this procedure. This showed that no appreciable back E.M.F. was produced by the combined actions of the light and the electric current.

(*b*) Again the cell was connected in one arm of the bridge illuminated and balanced. The battery current was then quickly reversed by a reversing key. There was no apparent change of resistance. If there had been any polarization practically its whole effect would have had to disappear in less than a second. This might have been regarded as sufficient proof of the non-existence of polarization. (*c*) Next a test was made to see if the decrease of conductivity in the Giltay cell took place independent of the action of the current during the period of illumination. It was found, for example, that the conductivity at any time after the cell had been illuminated for 2 min. 10 sec. was that shown in curve 17 whether the current was flowing through the cell during the first two minutes or not.

At another time two series of observations were taken, one with the current acting all the time and the other with the current off during the first 60 seconds. The results are shown in the following table, where the conductivity in the dark is represented by unity, and where the observations were taken in the order enumerated by the sets.

Remembering that the current flowing through the selenium cell when the above observations were made was from 20 to 100 times larger than it was during the previous observations when the pronounced decrease of conductivity in the Giltay cell by light was noted, and allowing for the inconstancy of the light source, it may be concluded that the light action is independent of the current.

(*d*) Fearing that some might raise the question as to whether the 10 seconds allowed for the resistance determination might not be sufficient time for the current to produce the decrease under discussion, a further

TABLE VI.

Conductivity of Selenium Cell after Being Exposed to Light.

Time of Exposure.	Conductivity without Current Flowing in Cell. Av. of Sets II. and IV.	Conductivity with Current Flowing in Cell. Sets III.
70 sec.	32.7	32.3
90 sec.	31.9	31.2
2 min.	30.7	30.3
	Set IV.	**Av. of Sets III. and V.**
70 sec.	30.5	30.7
90 sec.	29.9	30.0
2 min.	29.2	29.1
	Av. of Sets I. and III.	**Sets II.**
90 sec.	34.1	33.2
2 min.	32.9	32.2

test was made in which the mean time that the current flowed through the cell was 0.06 second. The pendulum before mentioned in this paper was used to first close the battery circuit for lighting the tungsten lamp when desired, then to close the battery circuit through the selenium cell and Wheatsonte bridge circuit, and 0.01 sec. later to close the galvanometer circuit for a period of 0.1 sec. The resistance of the cell was 640,000 ohms and the fall of potential across it was about 0.1 volt. The following are the observations:

Time of Exposure, Seconds.	Deflection without Current Acting.	Deflection with Current Acting.
0.5	43.0	43.3
1.5	67.5	66.9
2.5	68.8	66.9
3.5	70.1	—
5.5	66.9	67.5
10.5	64.9	65.3 and 63.2

As in the previous observations the conductivity is a function of the deflection. The slight differences in the deflections with and without the current acting can be explained by assuming that the selenium had not recovered by the same amount for all the observations.

It may now be considered definitely settled that the decrease as well as the increase of conductivity in the Giltay selenium cell no. 2 represents a genuine change in the selenium or what is supposed to be selenium and not what is ordinarily termed polarization.

It has been shown by a great many investigators that the sensitiveness of selenium decreases with increase of temperature. However it has not been shown to my knowledge how the conductivity for different times of exposure varies with the temperature. As questions in the theory are involved in such information, I have obtained data at different tem-

peratures for time conductivity curves. Such curves are shown in Fig. 6. While the observations are not very accurate, and the range of temperature is not very great, yet it is safe to draw certain conclusions. The conductivity in the dark is more than four times larger at 46.5° C. than it is at 11° C., and yet the maximum conductivity under the influence of intense illumination has nearly the same value. This is of course in agreement with the well established fact that the sensibility of certain selenium cells decreases greatly with rise in temperature. The maximum

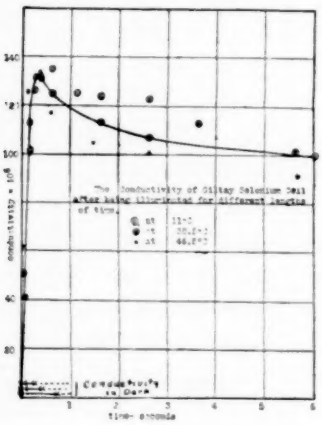

Fig. 6.

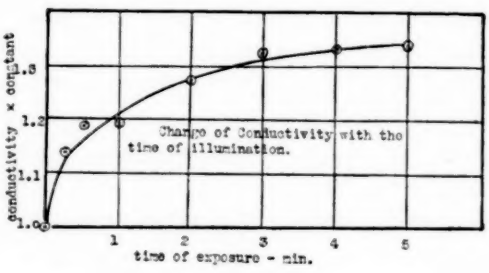

Fig. 7.

seems to be shifted toward the conductivity axis at higher temperatures. However there is reason for believing that the intensity of illumination was slightly less at the higher temperature than at 11° C.

Another class of light-positive selenium continues to increase in conductivity when it is illuminated. The selenium in the Bidwell and also the Ruhmer cells belong to this class. In Fig. 7 is shown how the conductivity varies with the time of exposure for a selenium cell of the Bidwell type. In this particular cell the resistance was only 8,000 ohms, and the sensibility was very low. The cell was not surrounded by a liquid while the readings were being taken; consequently a part of the observed change of conductivity may have been due to temperature. In Fig. 8 are shown similar curves for two other cells of this class.[1] Curve *I* is for a cell that was slowly cooled in the making process, and curve *II* is for one that was quickly cooled in

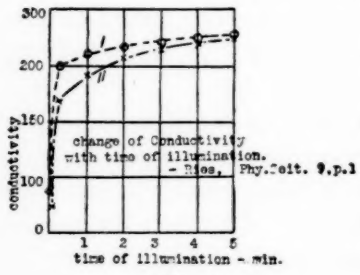

Fig. 8.

[1] These are taken from a paper by Ries, Phys. Zeit., 9, p. 9, 1908.

the making. He does not state the resistance of the cells or what was the intensity of illumination. For the cell referred to in Fig. 7, the intensity was that of a 16-cp. lamp at a distance 20 cm. When the intensity was greater than this the rise of the conductivity was more rapid at first and the final value was somewhat larger. In fact any light-positive selenium shows that the equilibrium value of the conductivity to increase with the intensity of illumination. Whether this equilibrium value varies in the same manner as does the conductivity for a very short period of illumination has not been investigated. Aside from the manner in which the "conductivity-time of exposure" curves differ in the two classes of selenium, there are two additional characteristic differences. The sensibility is much lower in the second class and the initial dark resistance is lower. At this time no special importance can be attached to the fact that the changes take place more slowly in the second class than in the first. The depth of the selenium and the intensity of illumination should be alike in order that such comparisons should be of particular value.

Experiments with Light-Negative Selenium.

Because of the difficulty of manufacture of selenium that decreases its conductivity upon exposure to light, I have not been able yet to determine the exact treatment of selenium that produces this so-called light-negative variety. In fact it took just as long and just as much patience to make the fifth sample as it did the first one. We shall therefore confine our attention to an analytical study of the behavior of these samples, particularly under the influence of light.

The general characteristics of this variety are not rigidly defined, except on a few points. The resistance is always small, and when the sample is first prepared it is very unstable. The smaller the resistance the greater is the sensibility, *i. e.*, the greater is the percentage change of resistance by light. Usually the amount of decrease of conductivity increases with increased illumination, but many times I have observed that a weak illumination such as the diffuse light of the room produces practically as great a change as does an intensity one hundred times as great. Generally the selenium recovers quickly when the light is removed, but after many exposures it may become fatigued and not recover for hours or at all. If the recovery is only partial then the sensibility is reduced. A few times and without any warning the selenium has for a single exposure become light-positive instead of light-negative. This was usually when the resistance was unsteady and when the selenium had been repeatedly illuminated. With one exception this reversal of effect has occurred only in newly prepared samples.

The following table will show the regularity of the increase of resistance of two samples which were about a year old. Unless otherwise specified the illumination was quite intense.

TABLE VII.

Table Showing by Successive Readings the Decrease of Conductivity in Two Samples of Light-Negative Selenium.

Sample No. 9. Time of Observation.	Resistance in Ohms. In Dark.	In Light.
3:09	107	107.2 in diffuse light.
3:14	107.6	108.6 intense illumination.
3:17	107.6	108.6
3:25	107.6	108.4
3:32	107.6	108.7
3:54	107.6	108.7
4:06	107.65	108.7
4:21	107.6	
	No. 2.	
	18.9	22.8 in diffuse light.
	21.8	24.0 in diffuse light.
	22.0	24.7 in diffuse light.
		25.2 20 cm. from 16-cp. lamp.
	22.7	23.2 20 cm. from 16-cp. lamp.

When first made these samples showed the same amount of increase usually, but not only did the resistance in the dark shift very suddenly and irregularly, but the amount of the change in the light was very irregular and at times zero. The irregularities were made more pronounced by sudden changes of temperature or by very intense illumination. Table VIII. shows how the resistance gradually increased as the temperature was successively changed.

TABLE VIII.

Resistance in Dark, Ohms.	Temperature, Degrees Cent.
117	20
123	5
153.5	−10
148	0
157	20
191	3
189	4.5
196	−7
190	2
181	8
167	20
154	39
183	45

From this table it is observed that the general tendency is for the resistance to decrease by raising the temperature and for it to increase by lowering the temperature, but that the net result is an increase of resistance. Not only is the process not a reversible one, but often a change of temperature in either direction increases the resistance. The irregularities were exaggerated by extreme or rapid changes of temperature. All that has just been said however applies only to samples that have been newly made. The increase of resistance of sample no. 1 at the above temperatures was of the order of 1 ohm. By suddenly changing the temperature up and down as indicated in the above table and by tapping the selenium with a thermometer the resistance was further increased to 481 ohms at 24° C. It was then exposed to the light of a well lighted room for several months during the summer. All the time it was immersed in paraffin oil in a similar manner to that described previously as in use for the Giltay cell. At the end of the summer the selenium had increased in resistance to 6,200 ohms and it was not measurably sensitive to light. But this was not the most surprising thing. After being removed to the dark for a period of about a month its resistance fell back to 675 ohms, where it was somewhat unsteady and after the current was allowed to flow through it for an hour it fell still further to 67 ohms. It was then light-sensitive as before and has remained so for several months.

The way that the conductivity of these light-negative samples vary with the time of exposure is shown in Fig. 9. The lower curve is for

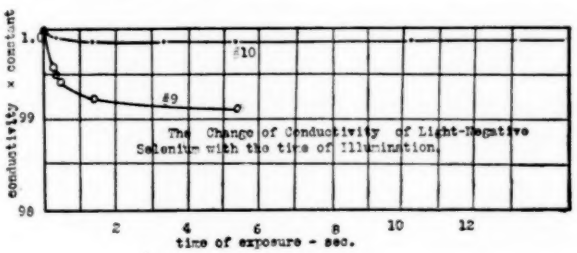

Fig. 9.

sample no. 9, which had a resistance of 107 ohms. The resistance of this sample was perhaps the most steady at all times of any that I have made. The upper curve applies to sample no. 10, which had a resistance of 312 ohms. It should be noted that almost all of the change takes place in less than a second. The intensity of the light was not much different from that used on the light-positive selenium which gave the results show in curves 15, 16 and 17. The rate of decrease in the latter

case is about 200 times greater than it is in the Giltay cell. Further experiments should be carried on with this light-negative variety, in order to determine the conditions of stability and instability.

RIES'S "ABNORMAL SELENIUM CELLS."

Ries in his paper on the "Effect of Moisture on the Electrical Properties of Selenium"[1] discusses a most peculiar variety of selenium which he has produced. When illuminated these abnormal selenium cells first rise to a maximum very quickly and then fall off slowly to a minimum value, very much as noted for the Giltay selenium cell. Sometimes the conductivity would even decrease below the conductivity in the dark. Two of his curves are shown in Fig. 10. The conductivity of these samples never increased much above that of the dark conductivity. The initial resistance and the intensity of illumination are not stated. He regards the decrease of resistance as a spurious effect which merely counteracts the positive light-action. His experiments indicate that moisture plays an important part in the formation and persistence of this variety. I have not yet succeeded in reproducing his so-called "abnormal selenium cells," but this is no doubt because I have not duplicated the exact necessary conditions. I should prefer however to call this variety a third or modified type of the light-positive variety.

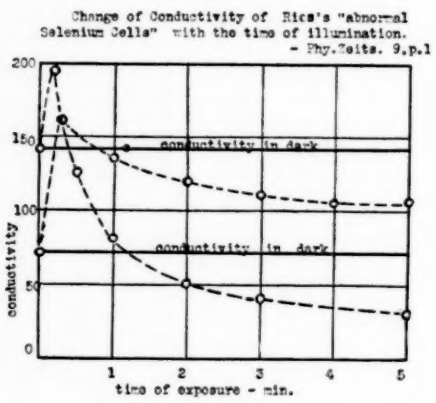

Fig. 10.

THE APPARENT FAILURE OF OHM'S LAW.

Ohm's law states that in an electrical conductor the current flowing is proportional to the difference of potential, assuming of course that all other conditions remain fixed. In all varieties of light-sensitive selenium this law apparently does not hold. As the voltage across the selenium is increased the current usually increases at a more rapid rate than it should. The amount of the change in the specific conductivity is sometimes very large. The curves in Fig. 11 show how the variation differs in the two classes of light-positive selenium. It is noted that in the Ruhmer cell the amount of variation is almost proportional

[1] Phys. Zeit., 9, p. 1.

to the voltage, while in the Giltay cell the variation decreases as the voltage is increased. The different high potentials were applied from 20 seconds to 1 minute before each observation was taken. It was suspected that the falling off of the effect in the Giltay cell was due to a decrease of the conductivity by the high potential much the same as is produced by light. This suspicion was strengthened by leaving the potential of 116 volts on the cell about a minute before taking the observation. It is seen that this point is below the curve. In other words, just as in the case of light the change of conductivity is a function of the time of application of the changing agent. The way that the decrease takes place is shown by the observations recorded in Fig. 12. This curve tells its own story when it is compared with the curves 16 and 17 in Fig. 5. There can be little doubt but that just as light produces a rapid change in the positive direction followed by a slow change in the negative direction, so are there corresponding changes produced by difference of electrical potential. In order to be certain that

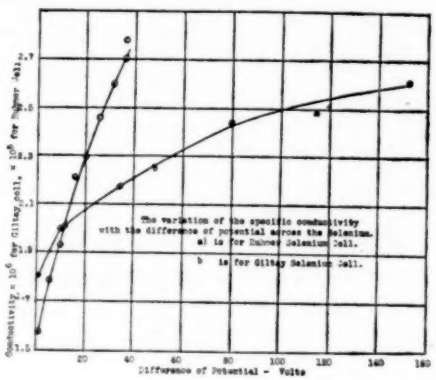
The variation of the specific conductivity
with the difference of potential across the Selenium.
a1 is for Hanover Selenium Cell.
b is for Giltay Selenium Cell.
Difference of Potential - Volts

Fig. 11.

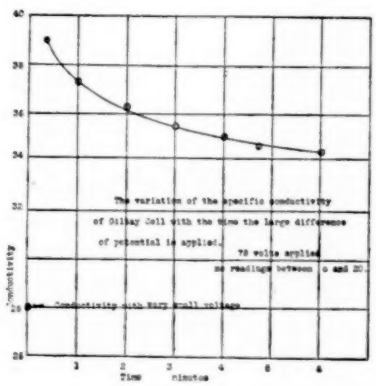
The variation of the specific conductivity
of Giltay Cell with the time the large difference
of potential is applied.
Time - minutes

Fig. 12.

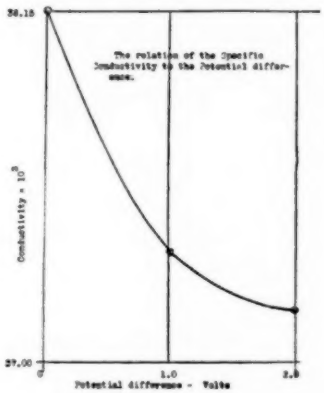

Fig. 13.

the variation first increased rapidly and then decreased slowly, the pendulum and ballistic galvanometer previously referred to were used. First the selenium cell was balanced in the Wheatstones bridge circuit where the fall of potential was two volts. Then the pendulum was

arranged to throw 120 volts instead of the 2 volts into the circuit for varying intervals of time. The galvanometer was in circuit during the last 0.1 sec. of the intervals. The deflection was a function of the change of resistance as usual. The relation of the change of resistance to the deflection may be estimated from the following:

$\Delta x = 600{,}000$ ohms, $d = 3.5$ mm.
$\Delta x = 650{,}000$ ohms, $d = 5.3$ mm.
$\Delta x = 700{,}000$ ohms, $d = 23.5$ mm.

The following table, IX., shows that the maximum conductivity was reached in about 0.1 sec. The increase is rapid and large in amount and the decrease is small and slow in taking place.

TABLE IX.

Time of Application.	Deflection, mm.	Time of Application.	Deflection, mm.
.01 sec.	1.0	.10 sec.	27.3
.02	5.0	.10	26.0
.05	10.9	.20	24.2
.01	1.5	.50	22.5
.02	2.5	7.0	3.5
.02	5.0	10.0	2.7
.01	1.2	60.0	2.5
.05	22.5	60.0	2.0
.10	27.1		

The variation of the specific conductivity of light-negative selenium takes place within quite a different range of potentials than it does for the light-positive selenium. Between two and ten volts I could not detect any variation whatever with certainty. But between 0.001 and 2.0 volts the effect of the variation of the potential difference was unquestionable. The curve in Fig. 9 shows the effect of varying the voltage on light-negative no. 9. The readings were taken after the potential had been applied about a minute. There was evidence that the change was a function of the time also. However this change was so small that it could not be clearly distinguished from a possible temperature effect. The important conclusion is that the electrical difference of potential changes the specific conductivity and in the same direction as the change by light. I have one low resistance sample of selenium that continues to show the light-positive characteristics at times. Also its specific conductivity increases with increase of voltage. Further experiments must be carried on with this sample.

DISCUSSION OF RESULTS.

On the basis of our explanation we have deduced four particular characteristic equations, which show the relations existing between the time

of exposure and the conductivity. These relations are shown in the curves in Fig. 1. Experimental results bearing on these relations with all the known varieties of selenium are recorded. The thickness of the selenium varied between 0.1 mm. and 1 mm. While the thicknesses are unquestionably greater than is permitted by the theory because of the absorption of light by selenium, nevertheless it seems that the general form of the conductivity-time curves should not be materially different from what it would be if the layer were very thin. Experiments have not yet been completed for the determination of the depth of penetration of selenium by light, but the indication is that the light penetrates much deeper than is generally supposed, particularly in the light-positive varieties.

The results showed, that the Giltay cell gave curves very similar to 1 and 2, that the cells of the Bidwell type gave data for a curve like no. 3, that the light-negative selenium led to curves of the character of no. 5, and that Ries's "abnormal selenium cells" led to a curve like no. 4. I may state that I found data for curves of no other character to be obtained, either from the theory or from any variety of selenium that has come to my notice. I regard the striking similarity between these experimental and theoretical curves as important evidence in favor of the proposed theory. It seems a waste of time to try to fit the comparison curves more accurately until further information is obtained concerning the depth of penetration of selenium by light.

The curves in Fig. 4 show that with increased intensity of illumination the maximum conductivity occurs sooner, that the maximum is much greater, and that the equilibrium value of the conductivity is correspondingly greater. Any view of the theory requires that the rates of change shall be a function of the light intensity. The curves in Fig. 3 show how the maximum should be shifted if the reverse changes were small in comparison with the direct changes. The form of the curves agrees with the experimental curves, and the maximum occurs quicker with increased intensity. Also for faint illumination the change of conductivity is almost proportional to the time of exposure. This agrees with the relation of the conductivity to the time of exposure as determined by Stebbins. But there is disagreement on two fundamental points, viz., this assumption will not account for the different values of the maximum conductivity or for the different values of the equilibrium conductivity, for different values of illumination.

The curves in Fig. 2 show the manner in which the conductivity should vary with the time for a given intensity of illumination when there are different amounts of the three components. This is again on the assump-

tion that the reverse changes are small. All the forms of curves obtained with the different varieties of selenium are included in these curves. Also there is agreement in the fact that the highest sensibility selenium is that of the highest resistance and that of the negative variety is that of the lowest resistance. There are no disagreements between experiment and theory so far as these curves are concerned, unless we introduce a fact to be explained in a later paper, *i. e.*, that the conductivity of the *C* kind is small in comparison with that of the *B* kind.

Knowing the nature of the disagreement between experiment and theory when the reverse changes were supposed to be small, one can see at a glance that the particular disagreements should be removed if the reverse changes were not neglected. By taking into account the reverse changes as explained in the theory we not only removed the above discrepancies and obtained the curves showing all the characteristics required by the experimental results, but we also had a method of explaining the initial amounts of the three components and for explaining the recovery of selenium. Just what the agreement between the sign and the magnitude of the ratio of the sensibility to the initial conductivity may be cannot be defined further than is shown in Tables I. and II. There is no evidence of disagreement on this point. Satisfactory proof is lacking however in that Table I. does not consider all the possible relations. Theory and experiment agree on the following with regard to selenium of the variety found in the high sensibility of Giltay cells; the maximum conductivity occurs quicker with intense illumination than with faint; the maximum increases in value as the intensity increases; the equilibrium value of the conductivity increases with the intensity; for faint illumination the change of conductivity is almost proportional to the period of exposure.

There are some instances where no relation can be traced between theory and experiment. The ordinary effect of a rise of temperature is to produce a change in the conductivity in the same direction as that by light. But in the high sensibility cell the change by temperature is opposite to that by light. But since the temperature effect is in the same direction as in the pure metals and of about the same magnitude, we may say that the temperature effect is metallic in nature and refuse to explain it further. It is well known that the temperature effect in selenium cells is extremely large ordinarily. The curves in Fig. 6 illustrate this. It may be that the negative temperature effect exists in all selenium cells and that it is sometimes concealed by the much larger reaction temperature effect in the opposite direction. However the greatest difficulty in this line is with the light-negative variety of

selenium. The change by heat is opposite to that by light and also to that in metals by heat. I have no explanation to offer further than to say that the indication is that the light and temperature produce entirely different effects in this variety of selenium, and the same effect in light-positive selenium.[1]

It is a noteworthy fact that in the Giltay cell a large potential difference produces a rapid increase in the conductivity which is followed by a decrease, almost identical to the changes produced by light except that the effects are not so large. As the two changes by light in the Giltay cells were found to be independent of the magnitude of the current one would naturally suppose that the large potential difference affects the conductivity as a result of electrical stresses in the selenium rather than as a result of the electric current. On this view the electrical forces would function in the dynamic equilibrium of the selenium.

Our experiments with selenium under pressure and those of Montén previously referred to show both a rapid and a slow change as noted for light and for high potentials. But the two changes here are difficult to measure accurately because of the simultaneous action of temperature. The equilibrium of selenium under pressure and temperature should be studied more carefully.

This dynamic equilibrium theory, if it satisfactorily explains all the observed phenomena, will still leave the whole subject in an unsatisfactory condition from one point of view. It will still remain to be explained why different varieties should have different rates of change. It may turn out that these different initial rates of change may arise from impurities which act as catalytic agents, or it may be if peculiar initial arrangements of the components are once established in the process of making, that there is an accompanying pressure or potential effect which maintains that peculiar arrangement. Some varieties of selenium do not have a fixed permanent stable equilibrium condition at once. They tend very slowly toward a new condition. In some cases moisture has been known to be the cause of such change but in others there is reasonable doubt. A semi-stable condition seems to exist in the light-negative selenium.

The way that light-sensitive selenium recovers when it is disturbed from its equilibrium condition by any agency is perhaps the strongest evidence in favor of the proposed dynamical theory. With the exception of some light-negative varieties of selenium, the selenium always recovers the conductivity that it possessed in the dark before illumination, and further

[1] On the similarity of the light and temperature effects, see paper by Miss L. S. MacDowell, PHYS. REV., 31, p. 524, 1910.

the two changes that appear during the direct action also appear in the reverse process. The conductivity time curves may be called the reciprocals of the same curves for the action of light.

If the view is accepted that the conductivity changes only when the amount of the conducting variety is changed, then there is obviously no discrepancy in Ohm's law.

CONCLUSIONS.

1. That light produces two changes in the conductivity of opposite sign in all light-sensitive selenium.

2. That the amount of the change is a function of the time of illumination as well as the intensity and character of the illumination.

3. That the selenium in the Giltay cell shows the same two changes under the action of high potential differences that it shows under the action of light.

4. That the character of the conductivity curves for the four known varieties of light-sensitive selenium can be explained by assuming the existence of three components in dynamic equilibrium, under given illumination, temperature, pressure and electrical potential differences.

5. That the effect of any agency that affects the conductivity of selenium is of the nature that it alters the rates of interchange between the components.

6. That the experimental results can be explained to a first order approximation on the assumption that only the B kind is conducting, of the three components which are in equilibrium according to the reaction $A \rightleftarrows B \rightleftarrows C$.

7. That if we accept the view here proposed the failure of Ohm's law becomes only an apparent and not a real failure.

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ON THE DISSOLUTION OF A METAL IN A BINARY SOLUTION, ONE COMPONENT ACID.

By Arden Richard Johnson.

ACCORDING to the law of mass action, as given by Guldberg and Waage, the velocity of a chemical reaction is proportional to the product of the concentrations, or masses, of the reacting substances. If we are dealing with the action of an acid solution upon a metal, then according to the above law either doubling the area of the surface of the metal in action, or doubling the strength of the acid acted on, will increase twofold the rate of the chemical action, or rate of evolution of hydrogen from the reacting system.

Fig. 1 illustrates diagramatically the meaning of the law when applied to the case of the action of metals on acids. Granted that we have in hand a metal and an acid solution between which there is possible a simple chemical reaction at any and all concentrations of the acid, then some point x on the diagram may represent the amount of hydrogen evolved for some particular concentration. Now according to the law of mass action, if the surface of the metal remains constant, a straight line drawn through x and the origin, O will represent the rate of chemical action at any and all concentrations.

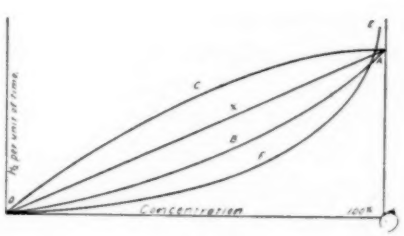

Fig. 1.

Stated analytically the law, for the case in hand, takes one of the following forms:

$$dx/dt = K\,(a - x)\,S, \qquad (A)$$

$$dx/dt = K. \qquad (B)$$

Formula A is the more general one, in which a is the original amount of acid started with, S the surface of metal exposed, and k the proportionality factor. The second formula is derived from the first, if we assume the invariability of the acid concentration and area of surface exposed by the metal.

It is obvious that it is assumed in deriving the expressions above that

the solvent used to vary the concentration of the acid must be an ideal one; *i. e.*, that the solvent must be absolutely nothing but a *diluting medium* for the acid.

However, to obtain such an ideal medium in practice is not an easy matter. *It is one of the objects of this work to discuss, in the light of experimentally obtained facts, those factors which cause the apparent divergence of theory and fact.*

For the sake of simplifying description and classifying subject matter I have divided into classes those factors, and agencies, which appear to me to have the greatest bearing on the dissolution of metals in acids.

(*A*) Physical or mechanical influences.	Products of reaction.	Action of gas.
		Action of solids.
	Viscosity of solution.	
(*B*) Chemical influences.	(*a*) Interaction of solvent and solute.	
	(*b*) Chemical effect of products of reaction.	
(*C*) Thermal influences.	Change of temperature during action.	
(*D*) Electrical influences.	Conductivity of solution.	
	Local circuits due to impurities.	

Hardly a solution can be found upon which one or more of these sets of influences do not have a powerful action upon results obtained; and in some cases these effects almost cover up any evidence of the working of the law of mass action.

If we assume that we have no other detrimental forces working than the mechanical, we see that under all possible conditions that are apt to be met with, the actual chemical activity observed must be less than that demanded by the law of mass action, *i. e.*, on referring to the diagram, page 1, we should obtain a curve something like *A*, *B*, *O*. It is obvious that the products formed are a gas and a salt, and perhaps some sort of a film upon the surface of the metal. If the gas formed does not readily escape as soon as formed, or if the salt formed is not immediately soluble or disintegrable by the mechanical action of the hydrogen, the action must of necessity be lowered. Likewise, if there is a tendency toward the formation of a film of oxide, or other material, the action must be diminished.

But if we take into consideration the chemical influences (secondary chemical action) which might be exerted by the products of the reaction, it would not necessarily follow that the action in the above mentioned cases would be decreased; for the solubility of the gas, or salt formed, in the acid solution might accelerate the action to a considerable degree. It is a well-established fact that the addition of a bit of some foreign salt, soluble in the solution, can considerably enhance, or retard, chemical action. Perhaps some chemists would prefer to call the influence of the small quantity of salt "catalytic" in character. The curve expressing

the relationship between chemical action and concentration might therefore fall either below, or above, as *A*, *C*, *O*, or, if we were particularly fortunate in the selection of our system, the curve might be a straight line.

There is, however, another concomitant in addition to the two just mentioned, which still farther complicates our problem, and that is the thermal effect accompanying the chemical action. We cannot have chemical action taking place without the simultaneous evolution or absorption of heat and a consequent change of temperature of the solution and metal.

The method used to eliminate as far as possible the effects of temperature will be dwelt upon more in detail later; suffice it here to say that such effects can be only approximately suppressed. In practically all of the cases under examination heat was evolved. While we do not know exactly the relations existing between rate of chemical action, quantity of heat evolved, and temperature produced, still it is quite safe to say that in most of the ordinary chemical reactions a rise of temperature causes a rise in the rate of the chemical action that is responsible for the evolution of the heat. Hence we may say that if the thermal accompaniments are considerable, all other conditions being ideal, the curve will fall above *A*, *X*, *O*, as *E*, *F*, *O*, and be more or less logarithmic in character.

While it is a fact that we understand a little, in a qualitative way at least, the effects of the above-mentioned influences and concomitants upon the working of the law of mass action, when applied to the action of metals upon an acid solution, yet in addition to these factors there is still another of very considerable importance in its bearing upon chemical activity, whose relation to the latter is not definitely understood. Nevertheless it is asserted by some that "*electrical conductivity*" is a "sine qua non" for chemical activity. *It is this alleged relationship between chemical activity and electrical conductivity which forms the main issue in this dissertation.* But to study this relationship itself, and to be able to draw trustworthy conclusions, requires a close study of the related influences and agencies already discussed.

To summarize as to the positive or negative effects of the principal influences upon the working of the law of mass action, as applied to solutions, I submit the following table: The symbol (−) means a depressing action upon the rate of chemical action; (+) an enhancing influence, and (o) no effect.

Influences.	Effects.
Mechanical.	−
Chemical (or catalytic).	+, or −, or 0.
Thermal.	+
Conductivity.	+, or −, (?) Is it necessary for *chemical action?*

DESCRIPTION OF APPARATUS.

Diagrams of apparatus used in carrying out the measurements of chemical activity are shown in Figs. 2–4. Fig. 2 shows the principal elements of the chief apparatus used. In the wooden rack (*A*) are arranged 11 graduated class eudiometer tubes in an upright position, closed end up. Each one of the eudiometer tubes dips into a glass beaker of 250 c.c. capacity, partly filled with water, oil, or mercury, as the case called for. *B* is a test-tube of 15 c.c. capacity which is so bent that it can extend into the beaker and empty under the eudiometer tube. Each test-tube is provided with a rubber stopper. The whole apparatus is

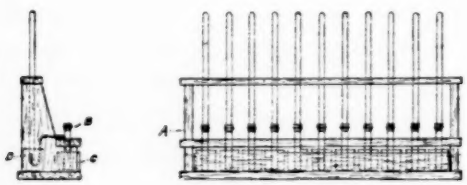

Fig. 2.

Fig. 3.

modeled after the Victor Meyer gas density apparatus. All test-tubes rest in the trough (*C*) which may be filled with H_2O for keeping down the temperature of the reacting solution and metal.

In using the apparatus each test-tube and its corresponding eudiometer tube was numbered from 1 to 11, from right to left, to prevent confusion and errors. Beginning with No. 1, which held 10 c.c. of 100 per cent. acid (or saturated solution), each succeeding test-tube to the left held 10 c.c. varying in strength from 90 per cent., by decrements of 10 per cent. to 0 per cent. acid or 100 per cent. solvent. The metal to be acted upon was cut from a rod of uniform diameter into small sections about 5 mm. long and 8 or 9 mm. in diameter. Both ends of the blocks were faced off smooth and then a rubber band stretched around the block as shown in Fig. 3, so that only the ends were exposed to the action of the acid. A block of metal thus prepared was placed in a certain test-tube containing the acid solution, the rubber stopper inserted, and after the first bubble of gas made its appearance at *D* the end of the tube was placed under the eudiometer and the gas collected for a known time consistent with accurate reading.

It is obvious that in cases where there is a tendency for a coating to form over the metal, or a layer of less concentrated solution in the case of slow action, some sort of shaking or stirring arrangement must be employed. Hence the apparatus shown in Fig. 4 was designed and used

in a few instances. It consists simply of a row of test-tubes inverted over small beakers and all fastened in a common holder so arranged as to allow of slight lateral motion controlled by the eccentric arm and motor (*A*). The mouths of the test-tubes were placed as close as permissible to the bottoms of the beakers. Each beaker with its filled test-tube contained the same volume of solution. The cylinder of metal to be acted on was first mounted in a piece of rubber tubing as shown (*B*) and then slipped under the mouth of the test-tube, and in this position received sufficient knocking about to keep the surface free from the objectionable features stated above.

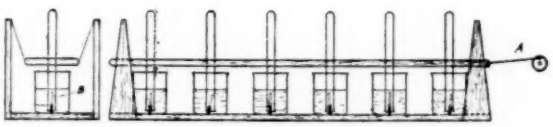

Fig. 4.

In order to study what relation the conductivity of a solution bears to the rate of dissolution of metals in the same, we must eliminate as far as possible the effects of those factors mentioned under heads *A*, *B*, *C*, page (—), as well as change of concentration of acid in solution during time of action, change of surface of metal exposed and decreased ability of solution for dissolving the salt formed. Practically the only way to do this is to *make the time for observing the rate of chemical action as short as is consistent with a reasonably accurate reading of the volume of gas evolved.*

Measurement of Conductivity.

All conductivity measurements of solutions were carried out by means of the regular Kohlrausch method. Care was exercised in all cases to thoroughly clean and dry the electrodes and cell with absolute alcohol and absolute ether, and dry in a current of air before each measurement. In practically all cases the measurements were made immediately before (and after) the measurements of the rate of chemical action, thus avoiding as much as possible changes in the conductivity of the solutions that might occur on standing.

Acid Solutions.

The acid used in most of the following experiments was glacial acetic, for the reason that it is not only a non-conductor when pure and attacks several metals, especially magnesium, with considerable avidity, but also because it is consolute at ordinary room temperature with a great number of both inorganic and organic solvents. Besides, most of the

acetates are somewhat soluble in both inorganic and organic solvents, particularly magnesium acetate.

Discussion of Curves.

The first curves we shall inspect are those representing the rate of chemical attack of magnesium by acetic acid dissolved in water, and the corresponding conductivity curves. The upper curve, Fig. 5, shows a

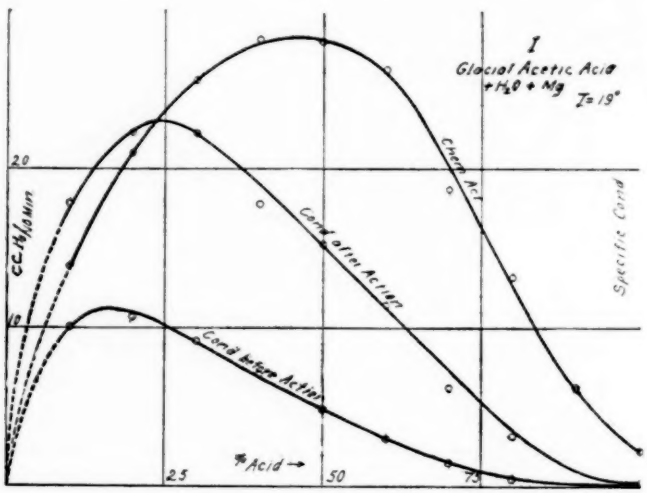

Fig. 5.

maximum chemical activity at about 45 per cent. acid. It will be noticed that the action is comparatively slow until a dilution of about 85 per cent. acid is reached, when the activity becomes quite considerable. Still it must also be noted that even for the pure acid the action is quite rapid.

The conductivity curves in Fig. 5 are seen to be very similar in character. However, these points are to be noted: The maximum of the conductivity curve (taken before chemical action) does not fall at the same concentration of acid as does that of the chemical activity curve; nor do the maxima of the two conductivity curves (before and after action) coincide. This latter fact points out how the addition of the products of chemical action effect the conductivity—indeed, we should naturally expect them to. Also, the great similarity of the conductivity and chemical activity curves in form would surely cause one to suspect some intimate relationship between the two phenomena.

We shall now examine some curves obtained with a solution of tartaric acid in HOH. A saturated solution was made up and continually diluted by decrements of 10 per cent. from the original strength. Fig. 6 shows

a definite maximum in the chemical activity curve corresponding exactly with that of the conductivity curve obtained after action. But the conductivity curve taken before action is different in that the maximum is not peaked, but rather flat.

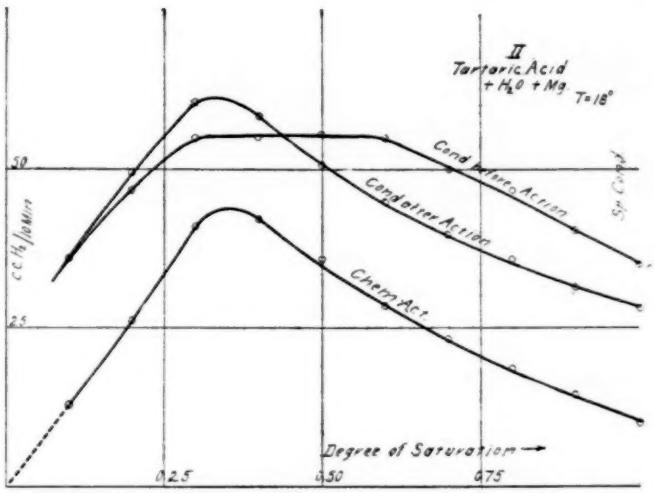

Fig. 6.

The curves in Fig. 7, obtained with the same acid, except that each solution was diluted to 33.3 per cent. absolute alcohol, show how differ-

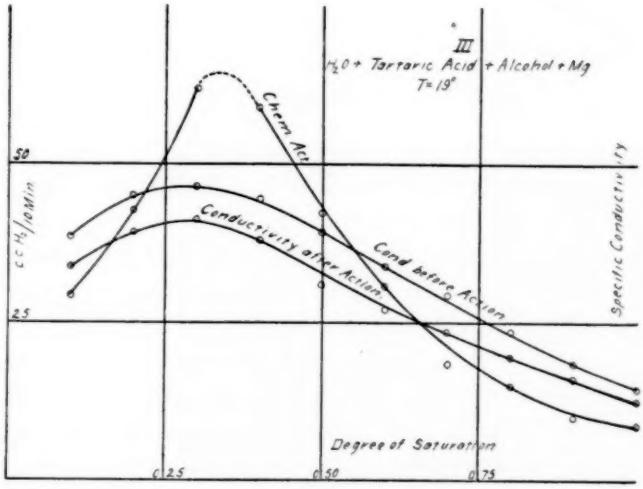

Fig. 7.

ently the character of the conductivity curve may become through the addition of a foreign substance, yet the chemical activity curve remains quite unchanged.

Of considerable interest are the curves obtained for oxalic acid dissolved in water forming ten sets of solutions varying from 10 per cent. of saturated to completely saturated solution at room temperature. The chemical action of this acid upon magnesium was very vigorous and a precipitate formed at all concentrations down to 30 per cent. of a saturated solution. But no crust formed on account of the great mechanical action of the hydrogen. It will be noted that these curves differ quite markedly from the preceding in that no maximum appears, and the chemical activity bears practically a linear relation to the acid concentration. So too is the conductivity curve quite parallel to the above curve.

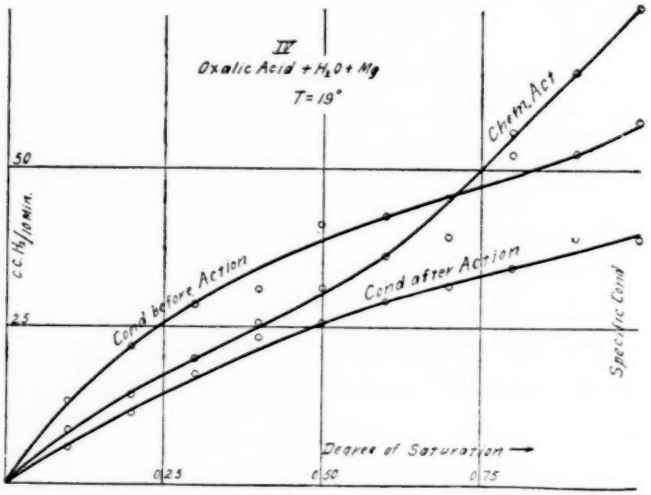

Fig. 8.

In comparing the last set of curves with those of acetic and tartaric acids, we are reminded that in the case of oxalic acid the influence of that force expressed by the law of mass action has been able to preponderate among the various factors effecting reactions and make itself evident. But why was its action so little in evidence in the two former cases? Here we should hardly guess that such a force was at work. If we turn back to the table of the various factors bearing upon the dissolution of metals in acids we shall see that neither the mechanical, electrical or thermal factors, under the conditions of the experiment, should interfere so powerfully with the working of the law of mass action. The solubility of the salts in all solutions is very great, the conductivities good and the thermal effect considerable. But as to the chemical influences alone! I think we are forced to agree with Dr. Kahlenberg's view of the chemical nature of solutions. As we gradually dilute acid with water, each step

of the process gives us a substance which acts as a definite chemical compound in entirety, and exerts a specific chemical affinity for the metal in hand. Hence we should expect such a function—changing of chemical properties with dilution—to disguise very materially the effects of the law of mass action.

But it may properly be asked here how the conductivity changes are so parallel to the peculiarly changing functions of concentration already noted. This matter will be discussed in detail later on.

We shall now pass from a consideration of the above data, which have been obtained with water as solvent, to those cases in which certain organic solvents were used.

Absolute alcohol, the "water" of organic chemistry, we see on examining the curves of Fig. 9, gave conductivity curves, when using acetic acid,

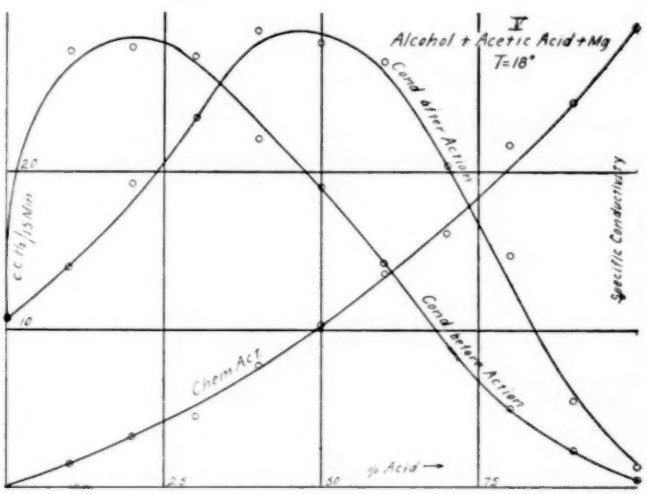

Fig. 9.

very similar in appearance to those obtained with water as solvent, but the chemical activity curve was almost a straight line, indicating that the effect of concentration is independent of the other factors. In this case we have changed the order of the magnitude of the conductivities of the various solutions in alcohol very much from what they were in the case of water, and while the chemical action shows up as a different sort of function yet the character of the curve expressing change of conductivity remains much the same. We might, however, explain this latter fact by assuming that the alcohol and acid interact, yielding H_2O as one of the products and this, acting on the acid, causes the similar electrical conductivity curve.

In ethyl-acetate as a solvent we have a strange state of affairs, in that, although the magnitude of the conductivity of the solutions is very small, still the curve representing the conductivity is very similar in character

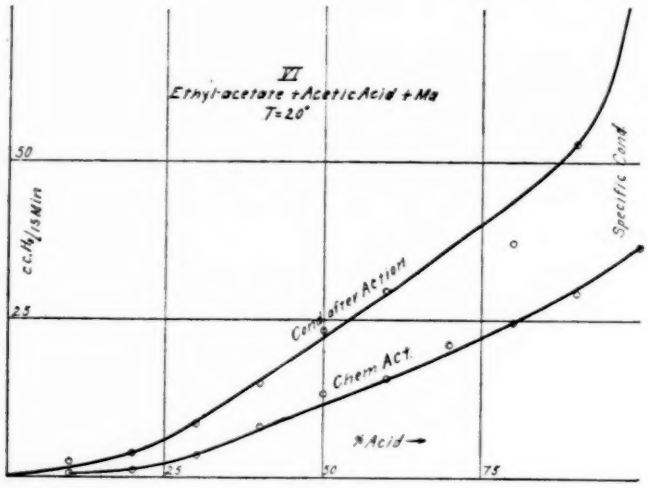

Fig. 10.

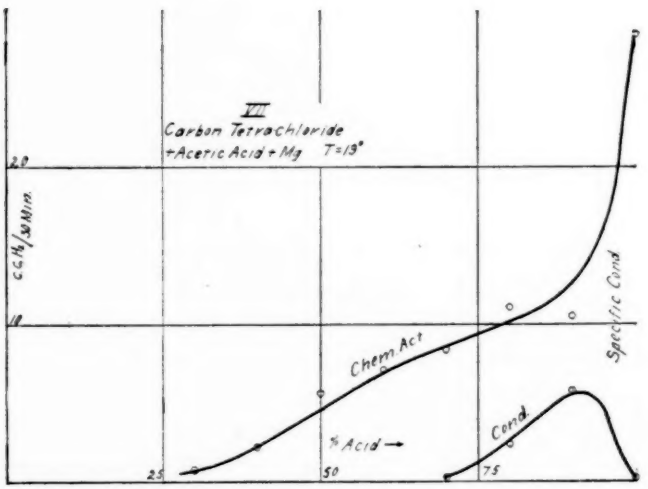

Fig. 11.

to the chemical activity curve and would cause one to suspect an intimate relationship between the two.

Carbon tetrachloride and also acetic anhydride used as solvents both yield very poorly conducting solutions, yet the chemical activity curves were obtained very easily. The rapidity of action in the case of the acetic

anhydride was quite considerable as the curve will show. However, in neither case is the conductivity anything like the reaction curve. In the case of the conductivity curve for CCl_4 a maximum was observed.

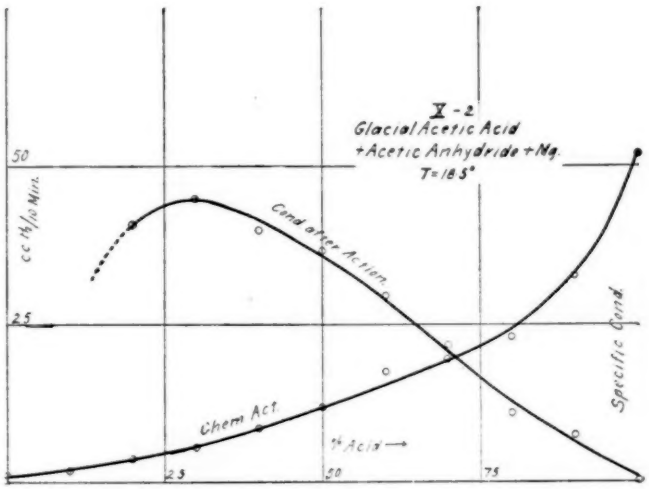

Fig. 12.

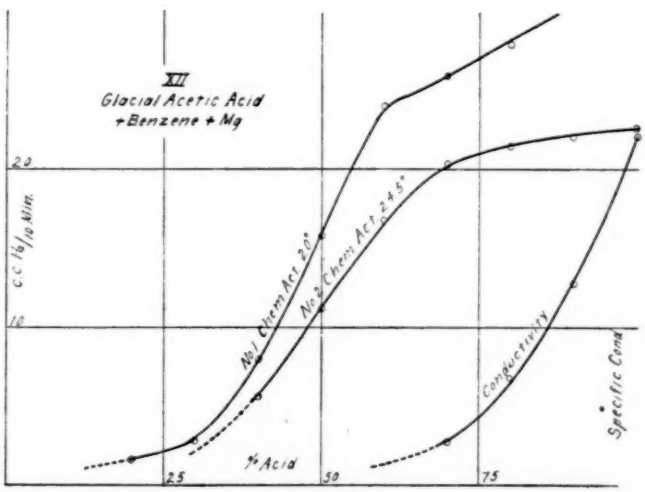

Fig. 13.

Such an event might be due to the presence of a trace of water dissolved in the solution. The validity of this argument will be treated of later. The chemical reaction curve for acetic anhydride is quite remarkable in that it is almost a straight line over most of its course.

A curve plate was obtained when using carbon di-sulphide as solvent

for the glacial acetic acid. Some trouble was experienced in that the two substances were not soluble in all proportions at the temperature of the room. The solutions obtained were of very low conductivity, and a

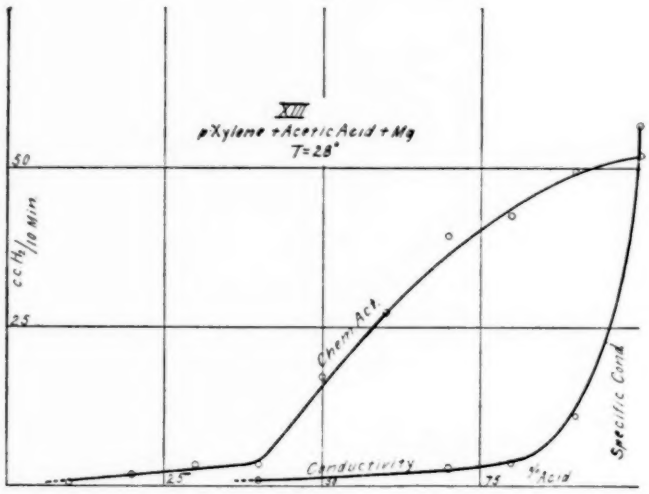

Fig. 14.

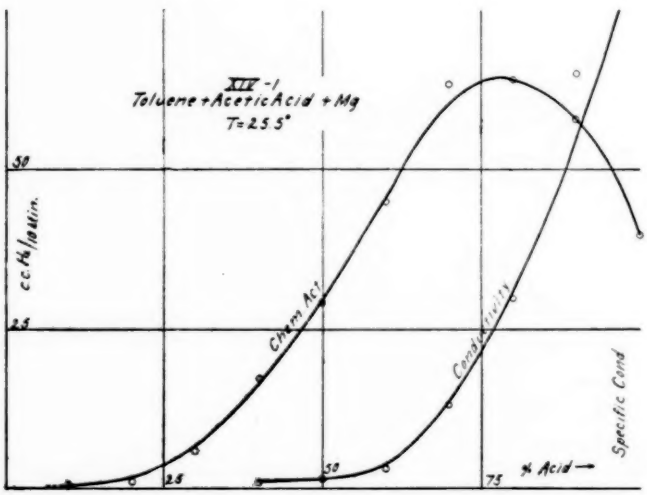

Fig. 15.

small addition of the CS_2 to the acid caused a very great depression of the rate of chemical action as shown by the curve. But the depression is really unduly great, partly because of the formation upon the magnesium of a rubber-like coating during the reaction.

We cannot maintain that the depression of the action in CS_2 solution

of acetic acid upon magnesium is due principally to the great depression of the conductivity in the face of the mechanical action of the products of the reaction. And this fact is farther borne out in the case of a solution

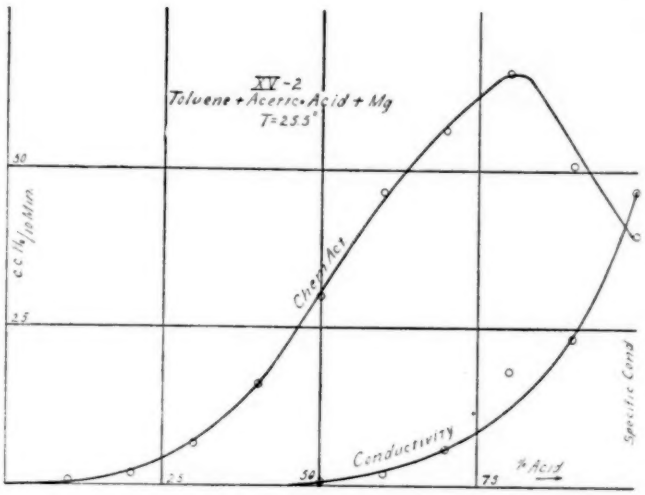

Fig. 16.

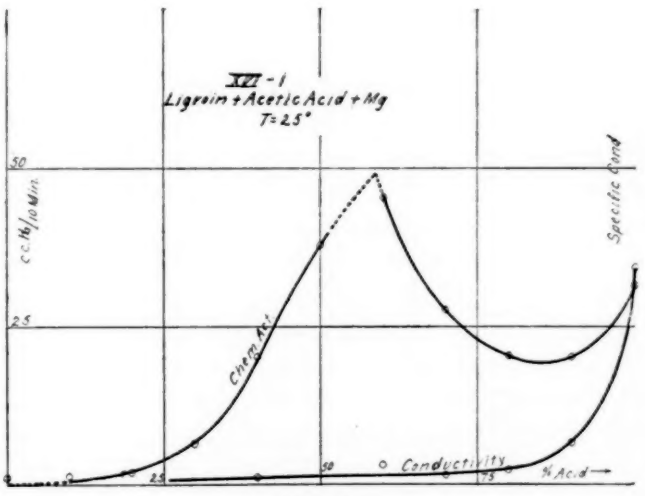

Fig. 17.

of acetic acid in di-ethyl ether, for here the fairly rapid chemical action persists to at least 75 per cent. acid concentration in spite of a tendency toward the formation of a sticky coating on the magnesium.

Benzene as solvent shows almost unabated action down to 60 per cent. acid. No film or precipitate could be noted at all so long as the solutions

remained at about 18°, but on raising the temperature a black coloration appeared which turned white on exposure to air.

Similar to the preceding is the working of p-xylene as solvent. This

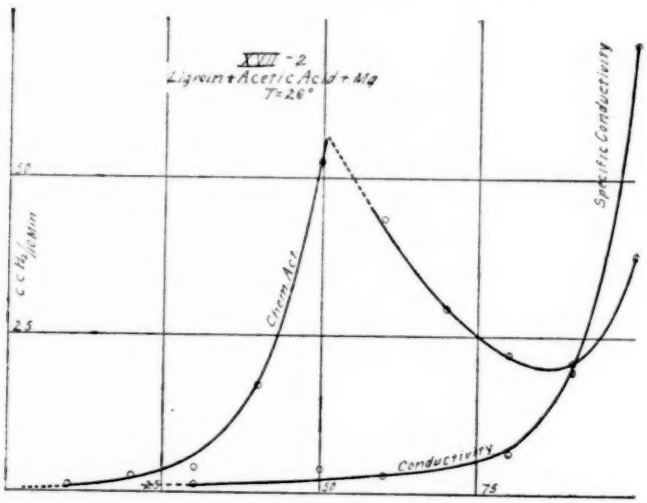

Fig. 18.

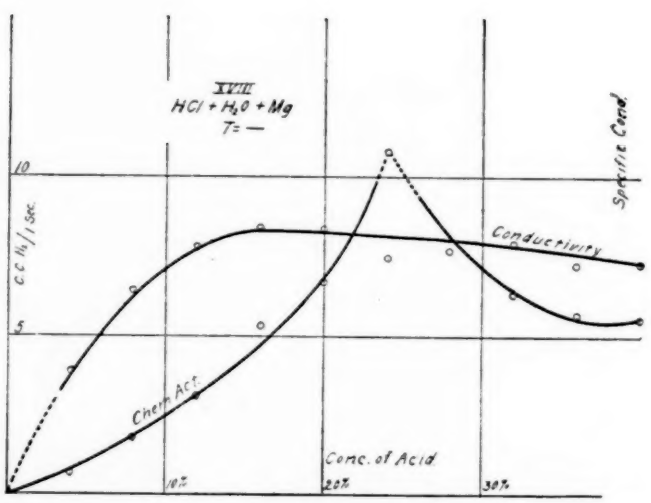

Fig. 19.

set of curves was obtained on a hot summer day and the black color appeared on the metal; still the action decreases only slowly to 60 per cent. acid.

After watching the course of results using these aromatic hydrocarbons as solvents it occurred to me that no trouble would be experienced

at all in getting entirely similar results using other hydrocarbons of the series and also aliphatic hydrocarbons. So toluene was next tried. But to my surprise the character of the chemical activity curve was quite different, in that instead of a depression of the reaction on addition of toluene an actual increase of action was noted. That is, a definite maximum was noted in the curve. This result was so surprising that a second entirely different sample was obtained and purified. But curve No. 2, Fig. —, testifies to similar results. The two curves are not absolutely alike, but are of a similar nature. Now this curve showing a maximum obtained when using an organic, non-conducting solvent for non-conducting glacial acetic acid is very interesting because it brings back to our minds a remembrance of parallel cases when acids are dissolved in inorganic, good conducting substances.

A still more striking curve is that obtained for the action of acetic acid, dissolved in ligroin, upon magnesium. This curve exhibits cusped portions and a maximum point, at first a considerable depression of the action, and then a rapid rise to a rate greater than for the pure acid, then a swift fall again. The figures for rate of chemical action are seen to be of no mean values, yet the results for electrical conductivity would appear to be rather discouraging to rapid chemical action in the light of prevailing theories.

Comparison of Chemical and Conductivity Data.

According to the prevailing electrochemical or ionization theory, we should rightly expect in most of these cases where factors *A*, *B* and *C* were favorable or neutral to chemical action, that the chemical activity and conductivity curves would be somewhat similar; and that for acid solutions of the same concentrations in different solvents, but of equal conductivity, we should expect rates of chemical action of the same order of magnitude. Yet an examination of the curves and data herein given will reveal no such regular relation. Solutions having extremely low conducting power are in many cases acted upon by the magnesium almost half as fast as in the comparatively good conducting aqueous solutions.

In order to facilitate a comparison of data for different solvents, Table I. has been arranged. After columns containing the names of solvents, temperatures and dielectric constants, are columns 1, 2, and 3, giving the average rate of chemical action, and average conductivity for all concentrations of acetic acid in a particular solvent. To obtain these average values the ordinates of the curves were added up and then the sum divided by their number.

It is worthy of notice that aqueous solutions of tartaric and oxalic

acids, while yielding fairly good conducting solutions, are not attacked any more readily by magnesium than are several other solutions of acetic acid in hydrocarbons. Even if we center our attention upon a single solvent we see that the magnitude of the conductivity can be varied within wide limits without appreciably effecting the rate of hydrogen evolution, all other conditions remaining practically the same. For example, compare the different values given for toluene, ligroin, and acetic anhydride.

TABLE I.

Solvent for Acetic Acid.	Temp.	Dielectric Constant of Solvent.	App. Av. Specific Conductance.	Av. H_2 Evolution per 10 min.
Water	19°	81.12	4545(−6)	86.95
Alcohol	18°	26.80	18(−6)	8.38
Ethyl acetate	20°	5.80	14(−6)	9.70
Ether	21°	4.36	——	7.04
Acetic anhydride	27°		8.5(−6)	34.78
Carbon tetrachloride	19°	2.25	8.0(−6)	1.97
Carbon bisulphide	18°	2.63	——	1.77
Benzene no. 1	20°	2.29	45.(−6)	16.17
Benzene no. 2	24.5°	2.29	45.(−6)	23.12
Toluene no. 1	25.5°	2.31	9.(−6)	31.31
Toluene no. 2	25.5°	2.31	5.(−6)	29.20
Ligroin no. 1	24°	1.85	2.(−6)	20.61
Ligroin no. 2	26°	1.85	6.(−6)	22.16
Xylene	28°		5 (−6)	22.56
H_2O as solvent of:				
Oxalic acid	19°	——	0.181	35.49
Tartaric acid	18°	——	0.03+	32.00
Tartaric acid plus alcohol	19°	——	0.016	11.90
Hydrochloric acid	——	——	1.735	2930.92

Be the above facts as they may, it appears as though we might center our attention upon the chemical activity curve and regard it as the *resultant* of all other curves expressing relationships between concentration of acid in solvent and all other forces, as: mechanical, thermal, electrical and others.

It is only proper that I close this dissertation by acknowledging my indebtedness to Dr. L. Kahlenberg, of the University of Wisconsin, for many suggestions in this work.

THE POSITIVE POTENTIAL OF ALUMINUM AS A FUNCTION OF THE WAVE-LENGTH OF THE INCIDENT LIGHT.

By J. R. Wright.

LENARD[1] was the first to investigate the velocity with which electrons are emitted from a metal plate in a vacuum when illuminated by ultra-violet light. He found that the velocities of emission were independent of the intensity of the incident light, but varied for different metals. He, therefore, concluded that the effect was a resonance phenomenon, the velocity with which the electrons were emitted being derived from the energy of the electron within the atom, the light playing simply a releasing role. More recently Ladenburg[2] investigated the relation between the initial velocities of emission and the wave-length of the incident light. He found that for a given metal the maximum initial velocities were directly proportional to the frequency of the incident light. Tests were made on the three metals, platinum, zinc and copper. Ladenburg and Markau,[3] by obtaining the velocity distribution curves, have shown that for a given region of the spectrum the electrons emitted have velocities lying within narrow limits. They, therefore, conclude that the photo-electric effect is purely a resonance phenomenon; the emission of the electrons will occur only when the frequency of the light bears a definite relation to that of the electron within the atom, and consequently for any given wave-length the velocities of emission ought to be all equal or closely grouped about a mean. The range of wave-lengths used by Ladenburg and by Ladenburg and Markau was from $\lambda 2700$ to $\lambda 2000$. Hull,[4] working in the region of very short wave-lengths, the so-called Schumann rays, found that the velocities of emission of electrons from a plate covered with lampblack increased with the frequency of the light, and concluded that, within the limit of accuracy with which this region of the spectrum is known, the proportionality discovered by Ladenburg holds for these very short wave-lengths. Three regions of the spectrum were obtained by means of absorption screens.

[1] P. Lenard, Ann. d. Phys. II., p. 259, 1900; VIII., p. 149, 1900.

[2] E. Ladenburg, Phys. Zeitschr., VIII., p. 590, 1907.

[3] Ladenburg and Markau, Phys. Zeitschr., IX., p. 251, 1909.

[4] A. W. Hull, Am. Jour. of Sc., XXVIII., p. 251, 1909.

The shortest wave-lengths of the three regions were approximately λ1710, λ1450 and λ1230. His conclusions are based on the assumption that the maximum velocities are due to the shortest wave-length in each region.

If the electrons, emitted under the influence of the light, are constituent parts of the atom, which owe their escape to resonance, then the velocities of emission can be determined by measuring the maximum positive charge acquired by a metal when illuminated in a perfect vacuum; for if m is the mass and e the charge of the electron, v the velocity of emission, and V the positive potential just sufficient to pull back the fastest electrons to the plate, then evidently

$$\tfrac{1}{2}mv^2 = eV \quad \text{or} \quad v = \sqrt{2Ve/m}.$$

The values of the positive potentials obtained by the earlier observers have ranged from 0 to 5 volts for different metals. Millikan and Winchester,[1] made determinations on eleven metals, obtaining values which varied from 0 for lead to 1.336 volts for silver. More recently Millikan,[2] working on the same metals and under identical conditions, found that by prolonged illumination with very intense ultra-violet light the positive potentials were increased from ten to thirty times the values previously obtained.

The importance of these results made it highly desirable that the relation between these new positive potentials and the wave-length of the incident light be determined. The investigation, the results of which are given in this paper, was undertaken with this object in view.

Two general methods were available for determining the velocities of emission; either an insulated plate, with earthed surroundings, is connected to an electrometer and the maximum positive potential, acquired by the plate when illuminated by ultra-violet light, measured, or the photo-electric current, which flows from the illuminated plate to an oppositely placed receiving plate, is observed, when a potential difference exists between the plates. The first method was adopted as more direct and better adapted to the object of the investigation.

The form of tube adopted and the arrangement of apparatus is shown in Fig. 1. The light from the spark passed through the spectrometer, fitted with the quartz lenses, L_1 and L_2, and the quartz prism, P, through the quartz window, Q, and fell upon the insulated aluminum plate, A, of 3 cm. diameter, which was connected to one pair of quadrants of a well-insulated Dolezalek electrometer, E. The electrometer gave a deflection of about 4 cm. per volt for a scale distance of 125 cm. G is a

[1] R. A. Millikan and Geo. Winchester, Phil. Mag., 6, p. 188, 1907.

[2] R. A. Millikan, Phys. Rev., XXX., 2, p. 287, 1910.

brass tube, blackened on the inside, and fitted with the two washers, w_1 and w_2, so arranged that practically no light fell upon the inside of the tube. G was kept earthed throughout the experiment, and was metallically connected to the gauze wire, g, which completely surrounded A. The two slits, s_1 and s_2, of the spectrometer were 1 mm. in width. In order to screen from electrostatic effects, the tube was entirely surrounded by the earthed metal case, M. The potentiometer arrangement, consisting of the two resistances, R_1 and R_2, and the batteries, B, was used to place a positive charge on A.

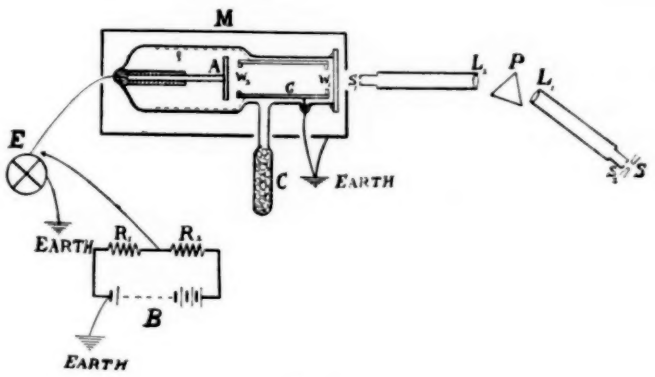

Fig. 1.

The source of ultra-violet light was a very powerful spark between metallic electrodes, the spark gap being about 2.5 mm. in length. The spark electrodes, with eight large Leyden jars in parallel, were made the terminals of the secondary of a large Scheidel transformer, the primary carrying 10 amperes at a P.D. of about 25 volts. Of several metals tested as electrodes zinc, cadmium, and iron were found to be the most efficient.

The vacuum was the best that could be obtained by the Dewar method. The tube was attached to a mercury pump, the bulb, C (Fig. 1) containing cocoanut charcoal being heated to 360° C. during the process of exhaustion. A glow discharge was passed from A to G for several hours in order to denude the electrode, A, as far as possible of occluded gases. The exhaustion was continued until a vacuum of approximately 0.00001 mm. mercury, as given by a McLeod gauge, was obtained. The tube after a period of six months, during which time the vacuum remained constant, was then sealed off from the pump and set up as shown in Fig. 1.

The method of observation finally adopted was to place on A, by means of the potentiometer arrangement, a positive charge and then illuminate with the ultra-violet light until the electrometer gave the natural leak

of the system, which was about 0.8 mm. per minute. This point was then observed and the positive potential necessary to give the same deflection measured. By this method of observation the period of illumination was greatly diminished, thereby preventing excessive heating of the spark terminals. This method was checked by comparison with that of direct observation, that is, by starting with A at zero potential and illuminating until the maximum positive potential was reached. The two methods were found to agree consistently.

During the preliminary observations the spectrometer was removed and the spark placed in the position occupied by s_1. The first observation on the positive potential with unresolved light gave a value of 0.25 volt. The plate was then illuminated by ten minute intervals for several hours a day during a period of three weeks. Frequent determinations of the positive potentials were made between illuminations. The positive potential was found to increase consistently with illumination until a value of 13.5 volts was reached, when further exposure to the light apparently produced no effect.

No claim is made that this value of 13.5 volts is the true maximum positive potential for aluminum. Without much doubt light reflected from the disk, A, will cause electrons to be emitted from the brass tube, G, which will flow to A under the influence of the electrical field. Moreover, as O. v. Baeyer[1] has shown, slow electrons will be very strongly reflected, which, as in the case of electrons produced by the reflected light, will tend to decrease the observed value of the positive potential. To what extent the positive potential will be influenced by these causes seems to be still an open question. Ladenburg and Markau (*l. c.*) found that prevention of reflection had an appreciable effect both on the value of the positive potential and the velocity-distribution curves, while Klages,[2] with a similar arrangement of apparatus, obtained results from which he arrived at exactly opposite conclusions. In the arrangement of apparatus used in the present investigation the only precaution taken to prevent reflection was the blackening of the inside of the tube, G. Since the chief object of this investigation was to determine the relation that exists between the positive potential and the wave-length of the incident light, a slight difference between the measured and the absolute value of the potential would hardly exert an appreciable influence on the results obtained. The problem of obtaining the absolute values of the positive potentials is being made the subject of a separate investigation in this laboratory.

[1] O. v. Baeyer, Verh. d. D. Phys. Ges., 10, p. 96, and p. 953, 1908.

[2] A. Klages, Ann. der Physik, IV., 31, p. 343, 1910.

Before obtaining the relation between the positive potentials and the wave-length of the incident light a determination was made of the rate at which the positive potential was assumed for any narrow spectral region. Starting with A at zero potential the deflection of the electrometer corresponding to the positive potential was read every ten seconds. Light of the mean wave-length 2166 from the zinc spark was used. The results are shown graphically in Curve I., the abscissas corresponding to the time and the ordinates to the electrometer deflections. On account of the heating of the spark terminals it was impossible to continue the illumination until the maximum potential was reached. The maximum deflection represented in Curve I. corresponds to a positive potential of 12.3 volts. The smoothness of the curve shows plainly the degree of accuracy with which observations on the positive potentials could be obtained under the conditions which existed throughout the investigation. Since the conclusions to be drawn from the positive potential curves (see V., VI. and VII.) must depend largely on the accuracy of the observations it was thought essential to introduce a curve illustrating this point. No further importance, than the above mentioned, is to be attached to Curve I.

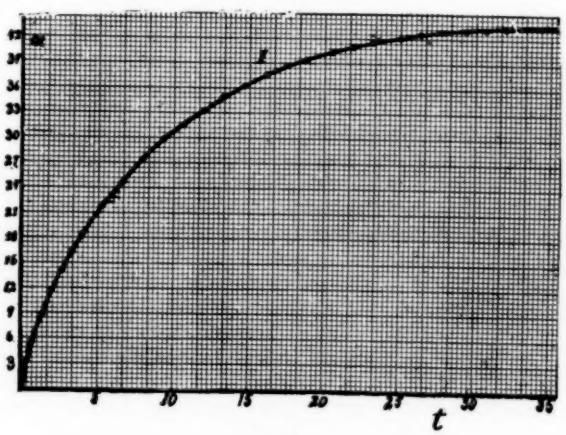

Fig. 2.

Tests were then made on the photo-electric sensitiveness of the disk, A, for light from different sources, the results for sparks between zinc, cadmium and iron being given in Curves II., III. and IV. respectively. The method of observation was that usually followed in such determinations. The disk was charged to a negative potential of ten volts, and then illuminated for one-minute intervals with light of different wave-lengths, and the corresponding electrometer deflections read. The wave-

lengths are plotted along the axis of abscissas and the electrometer deflections, which are proportional to the photoelectric current, along the axis of ordinates. The intensity of the light was kept as nearly constant as possible during these observations. A study of these curves in their relation to the positive potential curves will be taken up later.

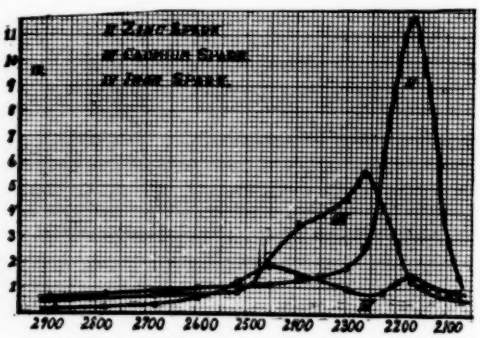

Fig. 3.

Determinations were then made on the positive potentials for definite wave-lengths in the region extending from λ2878 to λ2073. A typical series of results obtained in this manner, using light from the spark between zinc electrodes, is given in Table I., and represented graphically in Curve V. The ordinates of the curve represent the square roots of the positive potentials and the abscissas the wave-lengths. During the series of observations represented in Table I. the charcoal bulb was immersed in liquid air. Several sets of observations were taken without using liquid air, the only deviation from the above results being a lowering of the positive potentials by about 5 per cent. During any series of observations the intensity of the light was kept as nearly constant as possible, but no effort was made to keep the intensity the same for different sets of observations. On the contrary the length of the spark gap was purposely changed from time to time, and the current through the primary of the transformer was varied through values ranging from 8 to 15 amperes. The capacity in parallel with the spark was, however, kept constant during the entire course of the investigation. Photoelectric current curves were generally taken just preceding observations on the positive potentials.

A variation of the experiment was then made by using the light from the cadmium and iron sparks. The results are given in Tables II. and III., and represented graphically in Curves VI. and VII. A study of the Tables I., II., and III., and Curves V., VI., and VII. shows that contrary

TABLE I.

Zinc Spark.

δ	λ	V	$\sqrt{V}$
3° 48′	2,878	6.75	2.598
4° 48′	2,678	7.25	2.693
5° 48′	2,513	7.88	2.807
6° 48′	2,392	8.71	2.951
7° 48′	2,294	9.69	3.113
8° 18′	2,258	10.57	3.251
8° 48′	2,226	11.58	3.432
9° 18′	2,195	13.45	3.667
9° 48′	2,166	14.19*	3.767
10° 18′	2,139	13.77	3.711
10° 48′	2,113	12.99	3.604
11° 18′	2,092	11.96	3.458
11° 48′	2,073	11.19	3.345

δ = deviation (Na = 0).
V = positive potential.
λ = wave-length.
* = 14.19 volts = 2.23×10^8 cm./sec.

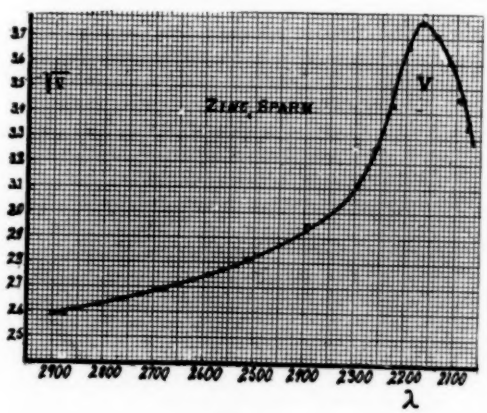

Fig. 4.

to the results found by Ladenburg and by Hull, the positive potential does not increase as a linear function of the frequency of the incident light, but reaches a maximum for λ2166. Using different sources of light is without influence either on the position of the maxima or on their numerical value. The slight difference in the numerical values of the maximum points may be ascribed to two causes: (1) observational errors, and (2) changes in the natural leak of the electrometer system, which varied slightly with weather conditions. The form of Curve VI. is

slightly different from that of Curves V. and VII. This variation is probably due, at least to a considerable extent, to the effect of the reflected light. Since the relative intensities of the light from the different sources varied considerably with the wave-length, it is to be expected that the effect due to the reflected light will also vary, thereby causing a slight variation in the measured positive potentials. Part of the

TABLE II.

Cadmium Spark.

δ	λ	V	$\sqrt{V}$
3° 48′	2,878	7.80	2.794
4° 48′	2,678	8.27	2.875
5° 48′	2,512	9.14	3.001
6° 48′	2,392	10.46	3.234
7° 48′	2,294	12.10	3.478
8° 18′	2,258	12.92	3.592
8° 48′	2,226	13.37	3.652
9° 18′	2,195	13.77	3.706
9° 48′	2,166	14.04	3.742
10° 18′	2,139	13.66	3.698
10° 48′	2,113	13.22	3.636

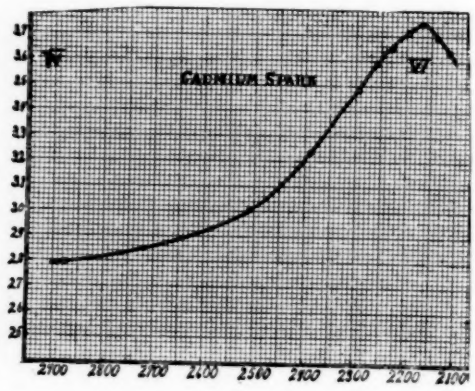

Fig. 5.

variation may, however, be due to the difficulty experienced in locating the points for wave-lengths ranging from λ2900 to λ2650. The readings around the maximum could easily be determined within 3 mm. in a total deflection of about 500 mm., while for the range from λ2900 to λ2650 the observational error was considerably greater, since for these wave-lengths the photo-electric sensitiveness was comparatively small, as is shown by Curves II., III., and IV.

TABLE III.

Iron Spark.

δ	λ	V	$\sqrt{V}$
5° 48′	2,512	8.59	2.931
6° 18′	2,448	8.88	2.980
7° 18′	2,347	10.09	3.176
8° 18′	2,258	11.13	3.334
9° 18′	2,195	13.01	3.604
9° 48′	2,166	14.16	3.759
10° 18′	2,139	13.61	3.688
10° 48′	2,113	12.93	3.597

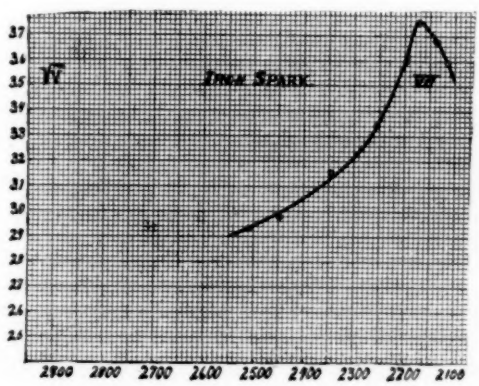

Fig. 6.

The complete independence of the positive potentials on the intensity of the light is evident from a comparison of Curves II., III., and IV. for the wave-length 2166 which gives the maximum potential for all three sparks. While the relative intensities of the light from the three sparks for this wave-length were approximately as 10 : 12 : 100 the widest variation of the positive potentials from the mean is less than 0.5 per cent. This is even more conclusively shown by other sets of observations in which the ratio of the intensities shows wider variation.

The lack of agreement between these results and those of Ladenburg and of Hull is probably due to some change that takes place on the surface of the metal during illumination. Whether this change is due to the breaking down of an electrical double layer of gas, or simply to a cleansing of the surface, or to a combination of causes, cannot be easily determined. That the emission of electrons from the metal under the influence of the light did actually cleanse the surface was without doubt the case in these experiments. The use of the disk as a cathode or a

discharge from an induction coil, during the early stages of exhaustion of the tube, had slightly tarnished the surface of the metal. After the disk had been illuminated for some time it was found that the part illuminated was decidedly brightened, presenting the appearance of freshly polished aluminum, while the unilluminated portion around the edge remained dark. That the increase in the positive potential from 0.25 volt to 14.1 volts can be ascribed solely to a cleansing process seems very unlikely in the light of the results obtained by Millikan (*l. c.*) on metals which were polished without oil, and had not been used as a cathode for an induction-coil discharge.

Whether other metals will show a similar relation between the positive potentials and the wave-length of the incident light is an important question which is being investigated at the present time by Professor Millikan and the author.

Before concluding, the author desires to express his thanks to Professor Michelson and members of the Department of Physics for the interest manifested in the work, and especially to Professor Millikan, at whose suggestion this investigation was undertaken, for many valuable suggestions.

SUMMARY OF RESULTS.

The positive potential of aluminum was found to increase from 0.25 volt to 14.1 volts as the result of long exposure to very intense ultraviolet light. The relation between this comparatively high positive potential and the wave-length of the incident light has been determined, and it has been found that, contrary to the results obtained by Ladenburg and by Hull, the positive potential reaches a definite maximum for $\lambda 2166$. Using light from different sources is without effect either on the value or the position in the spectrum of the maximum point.

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A METHOD OF MEASURING THE FLUCTUATIONS IN A RAPIDLY VARYING RESISTANCE.

By F. C. Brown and W. H. Clark.

SOMETIMES it becomes necessary to measure a variable resistance which changes during short intervals of time. We have found that by placing the variable resistance in one arm of a Wheatstone's bridge circuit we can express its average value for any interval of time in terms of the throw of a ballistic galvanometer where the galvanometer is thrown into the circuit by means of a pendulum for the desired interval of time which must be small compared to the period of the galvanometer. How small this interval should be is also determined by the rapidity with which the resistance changes. If the time is made sufficiently short the average resistance practically becomes the actual resistance at the middle of the interval.

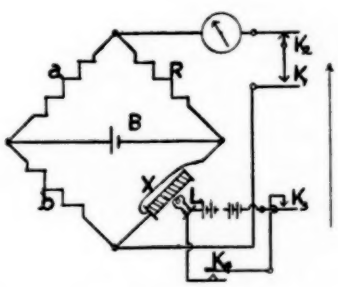

Fig. 1.

Theory.

The theory of the method is quite elementary. Consider resistances without appreciable capacity or self-induction to be connected in a Wheatstone's bridge circuit as shown in Fig. 1. Suppose the battery resistance to be small compared to the other resistances. Let the balance be disturbed by changing the resistance in the variable arm by a small amount Δx. Then it can easily be shown that the current through the galvanometer is

$$i = \frac{E(bk_2 + k_1aR)(\Delta x)}{(k_1x + k_2)^2}, \qquad (1)$$

where a, b, R and x and G are the resistances in the circuit,

$$k_1 = Gb + aG + bR + ab + aR,$$

$$k_2 = aRG + bRG + abR,$$

and

E is the electromotive force of the battery.

The quantity of electricity that is sent through the galvanometer may be expressed as

$$\Delta Q = i\Delta t,$$

or

$$Kd = i\Delta t, \tag{2}$$

where K is the constant of the ballistic galvanometer as obtained by discharging a known quantity of electricity through it and where Δt is the length of time that the current flows through the galvanometer. By combining equations (1) and (2) we obtain for the change of resistance,

$$\Delta x = \frac{Kd(k_1x + k_2)^2}{\Delta t E(bk_2 + k_1aR)}. \tag{3}$$

Now if Δx is small compared with x we may set

$$\frac{K(k_1x + k_2)^2}{E(bk_2 + k_1aR)} = C,$$

a new constant for a given set of resistances, and a given battery and galvanometer, and then

$$\Delta x = \frac{Cd}{\Delta t}. \tag{4}$$

The meaning of this equation (4) is that the change of resistance in the variable arm of the bridge is directly proportional to the deflection of the ballistic galvanometer and to the constant C, and inversely proportional to the interval Δt during which the galvanometer is in circuit. The change of resistance then can be calculated provided that it is small compared to the value of the resistance necessary to balance the bridge circuit. It will be noted that we have supposed that there is no appreciable damping of the galvanometer while it is in closed circuit during the interval Δt. The validity of this assumption will be considered later in the paper. Also the self-induction of the galvanometer is regarded as having no influence on the magnitude of the deflection.

Application to the Measurement of Small Changes of Resistance.—In order to test the linear relations between the deflection and the change of resistance and between the deflection and the interval Δt, known resistances were placed in the Wheatstone's bridge circuit shown in Fig. 1. The pendulum and keys were similar to those described in Carhart and Patterson's Electrical Measurements. A ballistic D'Arsonval galvanometer made by Leeds and Northrop was used. It had a period of 22.4 sec. A ballistic galvanometer with a period of 48.8 sec. was also used. To find the variation of the deflection with the change of resistance, the

keys k_1 and k_2 were placed a distance apart such that the interval during which the galvanometer was in circuit was $\Delta t = .05$ sec. Then the resistance in the variable arm was varied by different amounts previous to each reading. The readings were taken after the pendulum had operated the keys k_1 and k_2. In this test the resistance remained constant throughout the interval. All the observations that were taken are recorded in Curve III. of Fig. 2. It will be noted that there is only a small percentage error in any single observation and further that for a change of resistance as

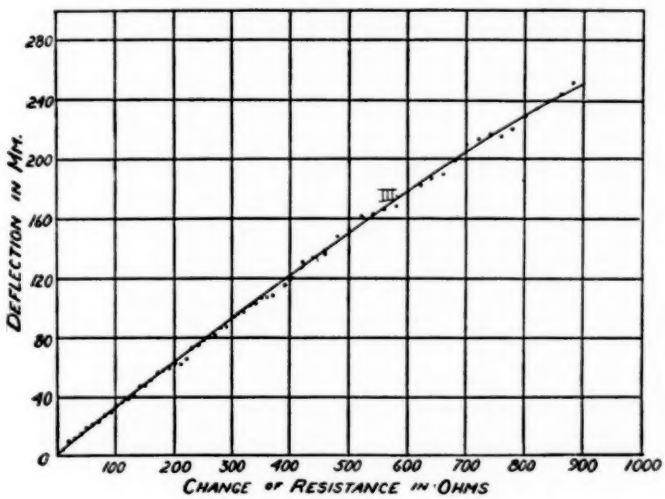

Fig. 2.

Relation between deflection and change of resistance; $a = 100$, $b = 100$, $R = 5000$, $x = 5000 - 4120$ ohms.

large as 800 ohms there is only a slight variation from the linear relation. For changes as large as $\Delta x = 200$ there is obviously complete agreement between the theory and experiment. It may be concluded here that the deflection is proportional to the change of resistance.

In order to test the relation between the deflection and the length of time that the galvanometer was in the circuit the variable resistance was changed a given amount, 15 ohms, from that required for equilibrium, and the distance between the keys k_1 and k_2 was varied. Observations were taken for both of the galvanometers referred to. These are shown in Curves I. and II., Fig. 3. Between .01 and about .12 sec. the linear relation required by equation (4) holds but from 0.12 sec. to 0.4 sec. there is a slight tendency for the deflection to grow less as the interval is increased. This slight downward bending of the time-deflection curves for larger intervals of time probably arises from the damping action of

the closed coil moving in the magnetic field, *i. e.*, the coil which required 5.5 sec. to move from zero to the end of the deflection had in the most unfavorable instance noted on the curve of Fig. 3 to move during the first 0.4 sec. with the coil closed through the Wheatstone's bridge circuit.

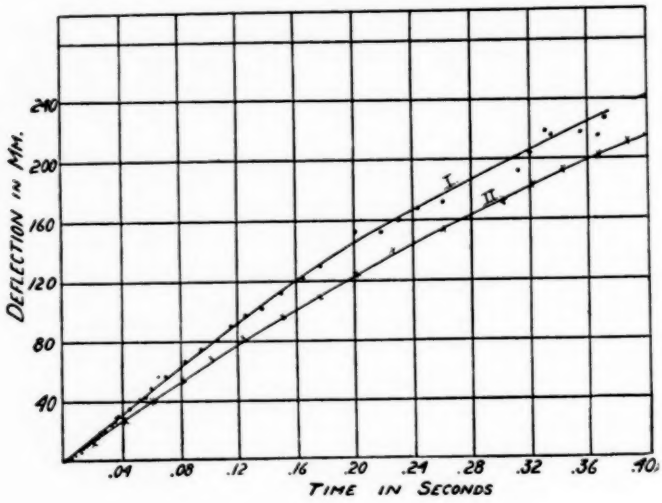

Fig. 3.

Relation between deflection and length of time the galvanometer is in the circuit. I. Galvanometer *E*. Period: 48.8 sec. II. Galvanometer *C*. Period: 22.4 sec.

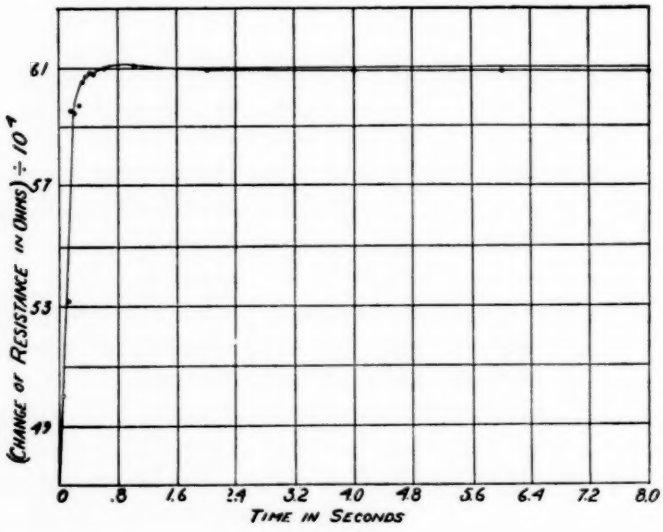

Fig. 4.

Change of resistanace of a Giltay cell with time of illumination. Resistance in the dark 673,000 ohms.

The amount of motion during this time, about one thirteenth of the quarter period, probably damped the coil appreciably. It was quite definitely settled that the linear relation between d and Δt was obeyed for values of Δt as small as .0075 sec. but for values less than this there was considerable doubt. The apparatus used seemed to give deflections consistently too small when Δt was 0.005 sec. It may be stated then that the method suggested for determining changes of resistance is applicable through the use of equation (4) for quite a large range of values for Δx and Δt. The value of the constant C can be computed or determined by experiment. It is hardly necessary to state that the range of applicability will vary to some extent with the apparatus used. There will enter such factors as the sensibility of the galvanometer, the value of the resistances in the circuit, and self-induction.

However, for small variations in resistance it may in practice often be simpler not to compute the change of resistance from the deflection, but to merely substitute known changes in the variable resistance which will give the same deflection that was obtained with the unknown variable resistance, or to obtain enough deflections with known resistances so that the value of the unknown change can be interpolated.

The Measurement of Large Changes of Resistance.—In case the change of resistance, Δx is large compared with the initial resistance x, equation (4) can not be applied and equation (3) is not easily serviceable. The change of resistance is a function of the deflection regardless of how large it may be, but it is not easily computed. We have found the easiest way out of the difficulty to determine the deflections given by the unknown resistance at different intervals of time and then to substitute various known resistances which would give a range of deflection covering those obtained by the unknown. The deflections together with the values of the known resistances were plotted to give a calibration curve. Then the value of the unknown resistance or the change of resistance was read from the calibration curve.

A simple illustration will explain this application of the method. A Giltay selenium cell was connected at x in Fig. 1. The selenium cell was placed in a dark box in which was also a tungsten lamp. By closing both the keys k_3 and k_4 the storage battery circuit was closed through the tungsten lamp. This illuminated the selenium cell. The method of procedure in the experiment was first to balance the selenium cell in the bridge circuit, after it had recovered, and then to set up the keys k_1, k_2, and k_3. Then the key k_4 was closed by hand. When the pendulum was afterward released it closed the key k_3 and illuminated the selenium cell. When the pendulum reached k_1, the galvanometer was thrown in

circuit, and when k_2 was reached the galvanometer was thrown out of circuit. The time between k_1 and k_2 gave the interval of time Δt. The time taken for the pendulum to pass from k_3 to the midpoint between k_1 and k_2 was considered the corrected time of exposure of the cell to the light. After the pendulum had thrown the key k_2, the key k_4 was opened by hand. If a period of illumination was desired that was greater than 0.60 sec., the absolute value of the period was not desired so accurately and therefore a crude auxiliary timing pendulum was used. The key k_3 was first thrown by hand and on the second the key k_4 was thrown, thus lighting the selenium and on any desired second the pendulum was released. This method kept the interval Δt constant and gave any period of illumination desired to a sufficient degree of accuracy. If the deflections by this method were too large they were reduced by changing the value of the battery electromotive force or by inserting resistances in series with the battery. Between each reading the selenium was allowed to recover.

The following table gives the observations that were made with the selenium cell.

TABLE.

Corrected Time of Exposure, Sec.	Deflections, mm.	Temperature.	Galvanometer Time Interval.
.05	7	24.8	0.05 sec.
.10	11	24.4	
.20	35	23.8	
.25	38	23.8	
.30	56	23.8	
.35	52	23.8	
.40	55	23.8	
.45	55	23.8	
.60	58	23.8	
1.00	61	23.8	
2.00	57	23.8	
4.00	56	23.8	
6.00	56	23.8	
8.00	55	23.8	

In the above observations the interval that the galvanometer was in the circuit was 0.05 sec. throughout. Using known resistance changes and the same interval 0.05 sec. data were obtained from which was plotted the calibration curve shown in Fig. 5. It will be observed from the calibration curve that for changes of resistance ranging in value from 500,000 to 564,000 ohms the deflection is almost a linear function of the change of resistance. For greater changes however the deflection changes very rapidly and becomes infinite when the change of resistance equals

the original resistance in that arm of the bridge. It is interesting to compare this curve with Curve III., Fig. 2. Both are deflection-resistance curves, but in Fig. 2 the change of resistance begins with zero while in Fig. 5 they begin with about 500,000 ohms. The resistances are of entirely different order of magnitude in the two instances.

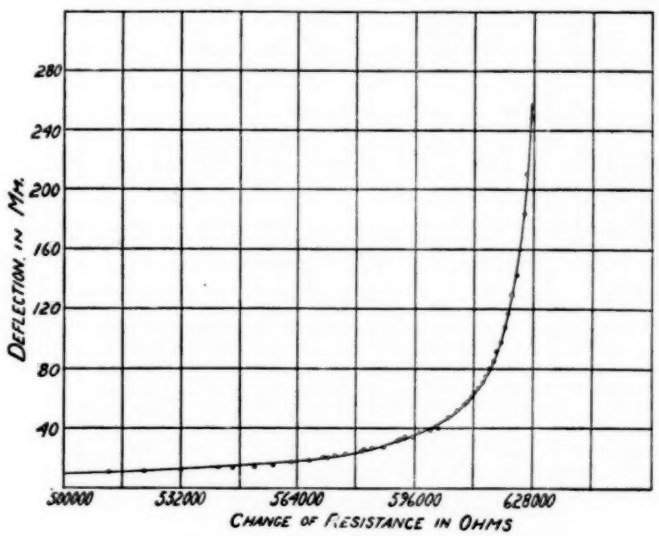

Fig. 5.

Calibration curve showing deflection for various known changes of resistance, when initial or equilibrium resistance is 632,000 ohms. Resistance in the other arms: $R = 6320$, $a = 1$, $b = 100$.

Using the values of the deflection obtained with the selenium cell shown in the accompanying table, we are able to determine the change of resistance from the calibration curve. The magnitude of the change for any time of exposure is shown in the curve of Fig. 4. The points on the curve each represent a single observation. The accuracy of a single observation is greater than we had expected. Almost without exception the points lie on the curve.

Other applications of this method may be found where it is necessary to vary the interval during which the galvanometer is in circuit and also the electromotive force of the battery. It may be stated in conclusion that the method is probably as accurate and as easy to manipulate as any method that has been devised for measuring such rapid fluctuations in resistance.

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INCREASE OF MAGNETIC INDUCTION IN NICKEL BARS DUE TO TRANSVERSE JOINTS.

BY E. H. WILLIAMS.

THE magnetic properties of very thin layers of iron and of nickel have been studied by Maurain.[1] He showed that these properties are different for the two metals. In the case of iron, the magnetization of very thin layers is much weaker than that of greater masses, whereas, in the case of nickel the opposite is true, that is, thin layers are much more strongly magnetic than thick layers. This difference is no doubt due to a difference in the molecular phenomena of the two metals and has an important bearing on the theory of magnetism.

Ewing and Low[2] have shown that the influence of a plane of transverse section on the magnetic induction of an iron bar is to produce a large magnetic resistance which, however, can be reduced by longitudinal pressure. Now, if the surface layers of nickel are more strongly magnetic than the mass of nickel, it would seem that, in this metal, transverse joints would tend to increase the magnetic induction rather than decrease it as in the case of iron.

In this investigation, the effects of surface layers in bar magnets of iron and of nickel, produced by cutting the bar in planes of transverse section, have been studied and compared under various conditions of field strength and longitudinal pressure.

The apparatus used was similar to that used by Ewing in which a short bar is brought to a condition of endlessness by sinking its ends in a massive yoke of iron which affords an easy path for the return of the lines of induction from end to end. The yoke was in the form of a ring, the outside diameter of which was 17 cm. and its cross-sectional area 24 sq. cm. The length of the primary coil was 8 cm. The samples investigated consisted of a rod of the material 1.27 cm. in diameter, and about 20 cm. long.

The bar was first tested without any cuts, after which it was cut in two in the middle and each end carefully examined to see that it was a plane before being put into contact again. The same tests were again

[1] Maurain, Jour. de Phys. (4), Vol. 1, p. 151, 1902.

[2] Ewing and Low, Phil. Mag. (5), Vol. 26, p. 274, 1888.

made, several series of observations being taken which agreed with each other very closely. The process was repeated for two and for four cuts.

The final results are shown in Tables I. to III., each table being the mean of four or more sets of readings which differed from each other very slightly. In Tables I., II. and III. are given quantities proportional to the magnetic induction. The absolute value of the magnetic induction is larger by the factor 30. It will be noticed that, in the case of iron (Table I.), transverse joints produce a decrease in the magnetic induction

TABLE I.

Iron. Magnetic Induction B/30.

H	Whole. Compression Kilos per sq. cm.			One Cut. Compression Kilos per sq. cm.			Two Cuts. Compression Kilos per sq. cm.			Four Cuts. Compression Kilos per sq. cm.		
	2	68	135	2	68	135	2	68	135	2	68	135
4	57.6	50.5	47.0	50.7	47.0	44.8	48.1	45.2	42.9	43.2	42.1	39.4
6	121.3	109.5	100.0	107.0	102.9	97.8	102.7	97.7	93.4	86.7	89.5	84.0
10	254.9	234.1	220.4	224.7	216.4	211.8	217.0	215.9	206.0	189.2	194.4	187.1
15	362.3	346.2	335.3	345.4	329.3	327.6	331.9	330.9	320.9	301.7	306.5	297.8
25	454.4	449.7	448.0	444.4	442.8	442.2	441.9	441.8	439.4	426.8	429.3	427.4
50	521.8	522.6	524.4	520.6	521.2	523.6	519.1	521.4	521.3	516.7	517.1	517.7
100	571.9	573.3	575.6	571.2	571.7	574.3	570.6	573.0	573.7	569.6	570.2	572.0
150	603.0	604.0	607.5	602.9	603.3	606.7	603.8	604.7	605.6	601.0	602.2	604.5

TABLE II.

Nickel—Sample 1. *Magnetic Induction B/30.*

H	Whole. Compression Kilos per sq. cm.			One Cut. Compression Kilos per sq. cm.			Two Cuts. Compression Kilos per sq. cm.			Four Cuts. Compression Kilos per sq. cm.		
	2	68	135	2	68	135	2	68	135	2	68	135
4	110.1	124.8	132.7	87.1	104.9	116.9	69.4	85.8	97.7	47.4	60.2	70.4
6	123.5	134.8	141.4	107.7	123.7	133.5	93.5	111.1	122.4	69.8	84.1	96.4
10	136.8	145.2	149.6	127.7	139.4	146.6	118.9	132.7	141.2	99.0	114.1	126.1
15	146.8	153.1	156.7	140.9	149.5	155.0	135.6	145.8	152.1	121.7	134.4	144.1
25	159.9	163.7	166.7	157.0	162.6	166.8	154.2	161.1	165.8	147.1	155.6	162.1
50	179.3	181.9	183.4	179.0	182.4	184.4	178.6	182.3	185.2	177.0	181.9	185.1
100	202.3	203.6	203.7	203.0	204.4	205.4	203.3	205.1	206.3	203.9	205.7	207.1
150	216.5	217.2	216.7	216.8	217.5	218.1	217.3	217.9	218.3	217.6	218.1	218.9

in all cases no matter what the value of the pressure or of the magnetic field, while in the case of nickel (Tables II. and III.), for field strengths greater than about 20 or 25 lines per square centimeter, depending on the pressure, the effect of the surface layers of the transverse joints more than counterbalances the effect of the magnetic resistance of the air gap, thus producing an increase in the magnetic induction.

An examination of Table I. will show also the Villari effect, that is, for field strengths below a certain value, increase of pressure decreases the magnetic induction, whereas for higher fields, it increases the magnetic induction. For this particular sample of iron the "Vallari critical point" occurs for a field strength between 25 and 50 lines per square centimeter. In another sample investigated it occurred for a magnetizing force considerably less. In the case of nickel (Tables II. and III.), the results, for field strengths up to 150 C.G.S. units or more, show an increase in magnetic induction for increase of pressure, which agrees with the literature on the subject. However, in the case of sample 2 (Table III.), the results indicate a "Vallari critical point" for a field strength between 150 and 200 C.G.S. units. While this effect is not very pronounced, yet the fact that it occurred in each of six series taken with the whole sample leaves no doubt that it exists.

TABLE III.

Nickel—Sample 2. Magnetic Induction B.

H	Whole. Compression Kilos per sq. cm.				Two Cuts. Compression Kilos per sq. cm.				Four Cuts. Compression Kilos per sq. cm.			
	2	68	135	210	2	68	135	210	2	68	135	210
4	108.7	113.7	119.0	123.3	67.9	80.3	88.5	95.6	47.0	57.4	66.1	75.0
6	117.4	121.7	126.5	130.4	90.8	103.5	111.2	117.5	68.0	79.9	88.7	96.3
10	127.2	130.8	135.3	138.9	114.7	123.2	129.6	134.5	96.7	108.4	117.2	124.5
15	135.2	138.5	142.6	145.9	128.2	135.4	140.6	145.1	117.6	127.3	134.4	140.5
25	147.5	150.3	153.6	156.7	144.7	150.2	154.8	159.2	140.2	147.5	153.5	158.3
50	169.2	170.7	173.3	175.8	170.6	174.7	177.3	180.8	171.8	176.5	180.1	183.3
100	197.2	197.6	198.7	199.7	200.1	202.0	202.9	204.6	203.3	205.1	206.3	207.3
150	214.6	214.2	214.1	214.5	216.2	217.6	217.6	218.1	218.3	219.1	219.3	219.8
200	227.2	226.0	225.5	225.2	227.3	227.7	227.6	227.5	228.6	229.0	229.0	228.8
250	236.9	235.7	234.7	234.3	236.0	236.9	236.3	236.4	237.3	237.3	236.9	236.8

The effect of transverse sections on the magnetic induction can be best seen by noting the per cent. change of magnetic induction due to these joints. For iron (Table I.), it will be noticed that this is a negative quantity, which indicates that transverse joints in a bar of iron tend always to decrease the magnetic induction by increasing the magnetic resistance. In the case of nickel the results, shown graphically in Figs. 1, 2 and 3, are very different. Beyond magnetic fields of 20 or 25 lines per square centimeter, the per cent. change is a positive quantity, that is, the effect of transverse joints is to increase the magnetic induction. Since the transverse joints produce a number of surface layers, and since, according to the results of Maurain in the article referred to above,

these surface layers are much more strongly magnetic than the body of the metal, one would expect to get an increase of magnetic induction provided the effect of the magnetic resistance due to the air-gaps were made less than that of the surface layers by increase of pressure, or the effect of the surface layers were increased by increase of the magnetizing force.

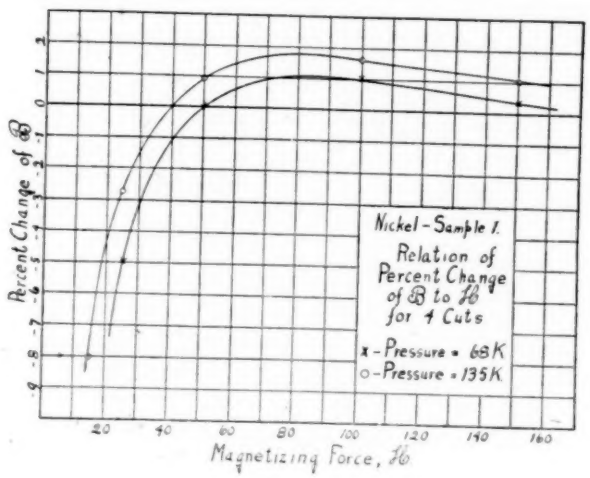

Fig. 1.

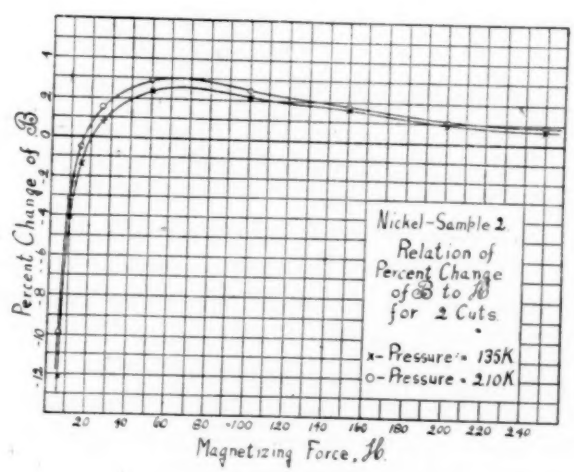

Fig. 2.

Both samples of nickel investigated were very soft as is evident from the comparatively high value of the magnetic induction produced by a magnetizing force of 4 C.G.S. units. Another sample which was very much harder produced little or no increase of magnetic induction due to

transverse sections. The value of B in this sample, for a field strength of 4 C.G.S. units, was only about one-third that of the samples given in Tables II. and III.

After the data on sample 1 had been taken and computed, it was noticed that the increase of magnetization reached a maximum value after which it fell off quite rapidly, as is seen from Fig. 1. In order to investigate this point still further, sample 2 was used in which the magne-

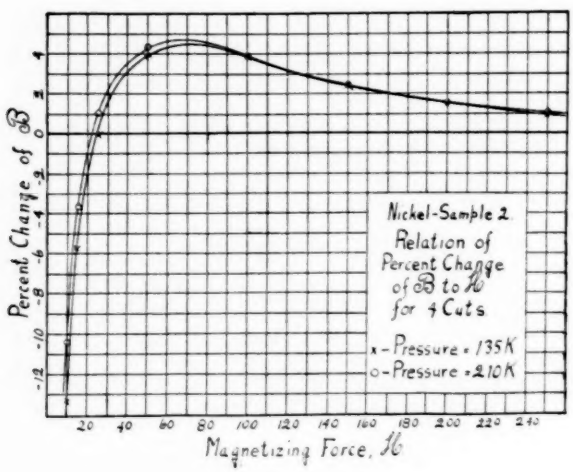

Fig. 3.

tizing force and pressure were carried to higher values. The same peculiarity was observed as in sample 1. From these results it is evident that the effect of the surface layers is due to two or more causes, and that it does not follow any simple law.

That the phenomena observed are molecular phenomena is quite apparent. Now, according to the electron theory, it appears that the elementary magnet of iron consists of two atoms while that of nickel contains six.[1] It is possible that in the surface layers of nickel where the forces binding the molecules together are weaker than in the deeper layers, only four, or even two, atoms form an elementary magnet, thus increasing the number of elementary magnets per unit volume.

In conclusion, I wish to thank Professor Jakob Kunz for suggesting this investigation.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
March 30, 1911.

[1]Kunz, PHYS. REV., Vol. 30, No. 3, p. 359, 1910.

ON THE FUSION OF CARBON.

By O. P. Watts and C. E. Mendenhall.

In a recent number of the Annalen, LaRosa[1] has described some experiments on the bending of carbon rods at high temperatures and has submitted this bending, together with certain peculiar surface appearances which he observed, as evidence for the existence of a true fusion point for carbon at ordinary pressures. It seemed to the writers that before accepting LaRosa's interpretation of his bending effects it would be well to make further tests with two points especially in mind, namely:

1. To compare the properties of graphite and carbon at high temperatures, to determine whether the bending was due to the traces of binding material (some hydrocarbon) remaining in the carbon, or whether it occurred equally well with graphite, from which the binder might naturally be supposed to have been largely removed by the prolonged and intense heating to which it had been subjected in manufacture.

2. To determine at least approximately the temperatures at which bending occurred, in order to decide whether it really indicated incipient fusion or whether it was merely an evidence of increasing plasticity at high temperatures.

Fortunately we had available a dynamo capable of giving continuously 600 amperes at 110 volts, direct current, so that we could use larger rods than LaRosa, and approach the bending stage gradually, giving ample time for the making of temperature observations on the rod with a Holborn-Kurlbaum type of optical pyrometer. Such observations give directly, of course, only the "black" temperature of the rods; to convert to true temperature we have used results connecting the "black" and "true" temperatures of carbon, shortly to be published by one of us.[2] We have made many tests upon rods 6 mm. in diameter, and 15 cm. and 30 cm. long, the material being (*a*) ordinary commercial carbon made by the National Carbon Co., Cleveland, O., U. S. A.; (*b*) an exceedingly fine-grained high-grade German carbon (Conradty) probably very similar to the material used by LaRosa; and (*c*) the purest graphite

[1] M. LaRosa, Ann. der Physik, No. 1, 1911, p. 95.

[2] Above 2000° C. the determination of this correction requires extrapolation of an empirical curve, so that the highest temperatures may be in error 50 or 75 degrees.

made by the Atcheson Graphite Co., Niagara Falls, N. Y. We produced bending either by pushing one electrode toward the other, or by rotating one electrode around a pivot near the center of the rod, or by hanging a weight on two equal rods clamped near to and parallel to each other and connected at their free ends.

Our results may be briefly summarized as follows:

1. American carbon takes a permanent bend most readily (Fig. 1, No. 3), German carbon next, and graphite with greatest difficulty. This

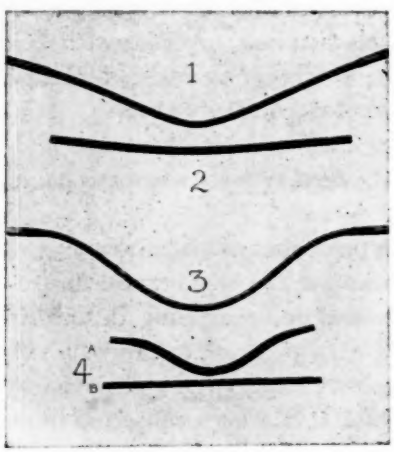

Fig. 1.

No. 1. Graphite. Angle of 50°. Max. temperature = 2770° C.
No. 2. Graphite. Broke hot, while bent 55° at center. 2630° C.
No. 3. Carbon. Angle 75°. Temperature 2600° C.
No. 4A. Rod expanded by carbon vapor. 2900° C.
No. 4B. Original size of rod.

is in the order of increasing purity, and decreasing amount of binding material. Nevertheless we easily obtained even with graphite more pronounced bending than any shown by LaRosa—as for example a sharp bend of 50° in the middle of a 30 cm. graphite rod (Fig. 1, No. 1) produced in four minutes at a temperature between 2700° and 2800° C.

2. The *lowest* temperatures at which bending has been observed are:

For an American carbon rod 1800° C.
For a German carbon rod 1900° C.
For a graphite rod 2150° C.

3. A rod bent while hot will permanently retain a much greater strain if allowed to cool while under stress. This is especially true of graphite, and below 2700° C. For example, one rod was given a 55° bend at 2630° C. in two minutes; it broke while hot and the pieces were almost

straight (Fig. 1, No. 2). Doubtless the *time* under strain will influence the amount of permanent set also. Up to 2500° C. graphite, though viscous as regards slow changes, is quite elastic for rapid changes and a loaded rod will vibrate freely.

4. In attempting to reproduce some of the other phenomena which LaRosa attributed to fusion, namely to obtain fragments of carbon having rounded outlines, and surfaces having a minutely globular structure, we proceeded in two ways: (*A*) Very regular and rather slow heating, obtained by keeping the current constant (about 400 amperes) while the rod or tube slowly diminished in cross section by burning and sublimation; and (*B*) rapid heating, obtained by suddenly throwing on from 300 to 600 amperes, according to the size of rod. In all cases we tried to remove contained gases by preliminary heating to 2000° C. or more.

Case A.—A one-fourth inch carbon rod would run from three to five minutes in the open air, the temperature gradually rising from $T_t = 2500°$ C.; conditions became unstable with considerable regularity at "black" temperatures of 3080° C. to 3250° C. (estimated at 3300° to 3500° C. "true" temperature), and an arc would be formed. The ends of such rods (or tubes) after arcing never presented any appearance of fusion, except that they were sometimes covered in part with a film or coating having a microscopically globular structure such as was described by LaRosa. Such surfaces were found, for example:

1. In the *cooler* parts of the *inside* of a graphite tube, heated to say $T_t = 3100°$ (in a vacuum) at the hottest part. In this case a layer .1 to .3 mm. thick has been *added* to the inside of the tube, reducing the inside diameter. This layer was considerably *harder* and finer grained than the original graphite.

2. On the *center* of the end of graphite rod used as the negative terminal of an arc, the arc playing around the edge of the end.

3. At various times as spots on the end of rod or tube which had arced, but not where the arc had been.

Case B.—Even with careful preliminary heating we frequently obtained violent explosions, undoubtedly due to rapid generation of carbon vapor in the interior of the rod. A further interesting result of this rapid generation of carbon vapor is the very pronounced swelling of carbon rods (less marked with graphite) which occurred with rapid heating (Fig. 1, No. 4). Though the temperature of the surface did not rise above 3000 to 3200° C. (true temperature) the interior was undoubtedly much hotter. A section of such an expanded rod is shown in Fig. 2, No. 1; the center is full of holes and crumbles at the touch, but has no appearance of fusion. A very peculiar effect due to the flow of carbon

vapor from the interior of the rod is shown in Fig. 2, No. 2. This nodulated surface presents every appearance of having been fused; yet it is to be noted that such appearances occur only on the outside (and hence cooler) part of the rod; they are more marked with large than with small rods (greater temperature difference between outside and inside); they occur at temperatures several hundred degrees lower than those at which, with slow heating, it has been found possible for a solid carbon or graphite rod to exist. (See above.)

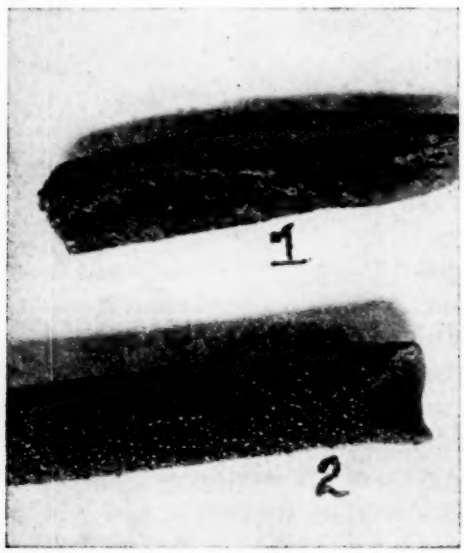

Fig. 2.

Therefore, while the surface appearances described at first sight suggest fusion, we are convinced that they are due in all our cases to condensation of carbon in the relatively cooler regions. The maximum temperature which can be obtained by electrically heating carbon is fixed by the sublimation point at the pressure used. Further increase of energy input after this point is reached simply goes into the energy of sublimination of the carbon. In a vacuum graphite tube furnace at a few millimeters pressure we have obtained in this laboratory a maximum (true) temperature of about 3100° C.; while with a carbon rod in air at 1 atm. pressure we obtained as high as 3500° C. With the same pyrometer a 250 ampere arc gave T_b = 3500° C., or T_t = 3800°. The difference between the arc temperature and the highest observed with a rod is undoubtedly the difference between the surface and interior temperature of the rod—the rod breaking down when the *inside* temperature reaches that of the arc.

Conclusion.

In view of the above experiments it seems reasonable to conclude that the bending of carbon and graphite at high temperatures cannot of itself be taken as evidence of incipient fusion—but rather as evidence of a gradually increasing plasticity; and while we cannot be sure that the peculiar surface effects observed by us and ascribed to condensation of carbon vapor are the same as observed by LaRosa, still their strong resemblance would lead us to suggest that probably the phenomena described by him were due to condensation and not to fusion.

University of Wisconsin,
April, 1911.

ON THE PRESENCE IN POINT DISCHARGE OF IONS OF OPPOSITE SIGN.

BY JOHN ZELENY.

SOME of C. T. R. Wilson's experiments[1] on the action of ions as condensation nuclei indicate that negative ions are present in the gas to which a point is discharging positive electricity; and similar results were obtained by Campbell.[2] Chattock and Tyndall[3] have considered a back discharge from the plane to be a possible explanation for the high values they obtained, from wind pressure, for the mobility of the negative ions in point discharge in pure hydrogen.

The following is an account of some experiments, in which dry air and hydrogen were used at different pressures, that were undertaken to find whether such ions of a sign opposite to that of the main discharge are present, at some distance from the point, in sufficient number to affect the electric field appreciably.

The method is based on the fact that when a wire probe, placed in a gas containing ions, is charged to a higher potential than that which it takes up of itself it cannot return to the latter potential if positive ions only are present, nor can it recover from an imposed lower potential if negative ions alone are present. Any leakage through the gas from a probe wire, placed near a discharging point and charged as stated, must be due to the presence of ions opposite in sign to that of the main discharge.

The accompanying figure shows the arrangement of the apparatus. The wire point B (diameter = .075 mm.) discharged to the plate D (distance = 14.8 mm.) above which the probe wire C (diameter = .26 mm.) was placed, usually at a distance of about 1.5 mm. but in some of the experiments at 6 mm., with like results. This probe wire was charged 200 volts or more above the equilibrium potential assumed by it when a given current was flowing between the point and plane, and its rate of leak noted on a voltmeter joined to it. The rate of leak for a like potential was then taken with no current flowing from the point to test the insulation of the supports.

[1] C. T. R. Wilson, Phil. Trans., 192, p. 403, 1899.

[2] N. R. Campbell, Phil. Mag. (6), 6, p. 626, 1903.

[3] A. P. Chattock and A. M. Tyndall, Phil. Mag. (6), 19, p. 449, 1910.

No appreciable leak of the probe, that could be ascribed to the ions in question, was observed in dry air at pressures between one atmosphere and half an atmosphere with steady discharge currents of either sign up to 7 microamperes in value, the largest that permitted the taking of observations at these pressures. By comparing the slowest leak detectable with

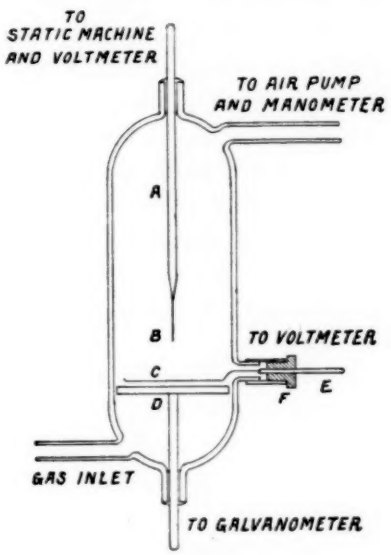

Fig. 1.

the rate at which the probe assumed the equilibrium potential after being earthed, an estimate was obtained for the upper limit of the number of these ions present and this shows that they must compose less than one fiftieth per cent. of all the ions.

Discharge Current in 10^{-6} Amperes.	Rate of Leak from Probe.		
	Negative Discharge.	Positive Discharge.	
0	.08 volts per sec.	.08 volts per sec.	Support insulation
.4	.25 volts per sec.	.40 volts per sec.	leakage.
7.	1.0 volts per sec.	1.6 volts per sec.	
15.	7. volts per sec.	12. volts per sec.	
29.	100±. volts per sec.	very fast.	Glow on plate with negative discharge.

With pressures less than half an atmosphere a leak from the probe was observed; at the higher of these pressures, with large discharge currents only, but with all currents at the lower pressures, of which the lowest used was 3 cm. of mercury.

The preceding set of readings with the air pressure at 17.6 cm. will

illustrate the nature of the results. Some idea of the numbers obtained at other pressures may be formed from those given by taking the leakages very roughly inversely proportional to the pressures.

The potential of the probe was in each case over 1,000 volts, and the capacity of the probe and electrometer was about 50 cm. To get an estimate of the relative number of the two kinds of ions present in this case, a capacity was added to the probe system and the rates at which the potential changed were measured when the probe was on the average 250 volts above and below its equilibrium potential. With a positive discharge current of 7 microamperes, for which the potential of the point was 3,600 volts and that of the probe 900 volts, the rate of charging was over 250 times as fast as that of discharging, showing that the ions of opposite sign to the discharge current were less than half a per cent. of the total number present. For the larger currents, however, they were relatively more numerous, as the leakages increase more rapidly than the discharge currents.

It will be noticed that the number of negative ions in the positive discharge is greater than the number of positive in the negative discharge. This is somewhat remarkable since with the largest current used above there was a visible glow on the surface of the plate with the negative discharge and none with the positive. It would seem that this luminosity is not an accompaniment of an ionizing process but may be caused by the impacts of negative ions against the molecules of the gas wherever the ionic velocity is sufficiently great, a potential drop at the surface of the plate being supposed in this case. Such a view would help account for the fact that the light at the surface of a point discharging negative electricity extends some distance into the gas while in positive discharge the light is much more confined to the metal surface.

Observations made at night failed to detect any glow on the surface of the plate when a non-intermittent positive discharge was passing with the gas at any of the pressures used, although with the negative discharge a faint glow was noticed for the largest currents used even when the pressure was as high as half an atmosphere.

In some experiments which were made to see if luminosity may attend recombination, the ions from two points, one discharging positive and the other negative electricity were sent from opposite sides into the space between two earthed gauzes or metal rings but no light effects were seen even with the gas under a greatly reduced pressure.

The results on probe leakage in electrolytic hydrogen were similar to those for air except that the leakages observed were somewhat larger and no glow was observed on the plate for either discharge.

In general then, the experiments show that while at lower pressures and especially in the larger currents there is a considerable number of ions in the gas, of opposite sign to that of the discharge, nevertheless, for pressures down to as low as 15 cm. and with currents up to 7 micro-amperes at least, these ions are not sufficiently numerous to affect the electric field appreciably.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
March 17, 1911.

NOTES ON OPTICAL PYROMETRY.

By C. E. Mendenhall.

THE following notes describe certain small and rather obvious modifications in existing instruments and methods, which however have been found so convenient that a brief account seems worth while.

1. A convenient mounting for using rotating sectors directly on the Holborn-Kurlbaum pyrometer for cutting down the initial intensity of the light from the hot body, and thus extending the range of the pyrometer. The usual method of accomplishing this is by means of absorbing or reflecting glasses mounted in front of the pyrometer objective, and the determination of the effective absorbing power of the glasses is a matter of some trouble, and it is moreover greatly altered by change in the angle of incidence and by dust. The arrangement of motor, shaft and sectors is clearly shown in Fig. 1; a common battery motor is fixed at the main

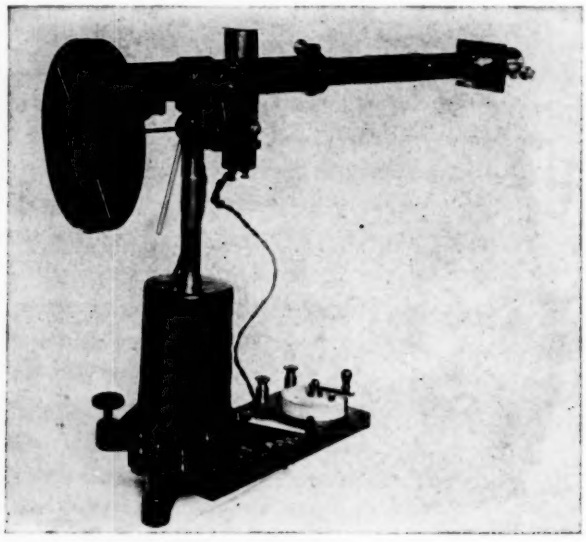

Fig. 1.

pivot of the pyrometer, and with a little care in balancing the disc and armature there is no noticeable vibration. The sectors are 13.5 cm. in diameter, and with this size openings as small as 3°, giving a reducing factor of 1/120 for one opening, may be used. It is very easy to have a number of sectors so that any desired reduction may be obtained.

2. A method of calibrating the Holborn-Kurlbaum pyrometer using but *one* known temperature and a number of sectors to give a number of reduced effective temperatures. Thus if a black body at the temperature of melting palladium, 1549° C., is used, and observations taken first direct and then with sectors having apertures of ½, ¼, ⅛, 1/20, 1/60, 1/120, corresponding effective temperatures are obtained from about 1450° to 1030° C.

These effective temperatures are calculated from Wien's logarithmic isochromatic, using $C_2 = 14{,}500$ and $\lambda = .658\mu$ as the wave length of effective transmission of the standard red glass used with the pyrometer. The transmission band of this glass is, however, fairly broad, about $.02\mu$, and one naturally raises the question whether the use of Wien's equation (and therefore this method of calibration) is justified, since the equation applies to monochromatic light. We have carefully tested this point in two ways—first by comparison of observations on a black body whose real temperature was 1063° C. (gold point) and on another whose effective temperature, reduced by sectors from 1546° C., was computed to be the same. These observations checked to about 2° C.—which is about the limit of accuracy of ordinary optical pyrometry. A further test was obtained by comparing observations, at various effective temperatures, obtained with the usual red glass eye-piece and with the spectroscopic eye-piece described below. With the latter, having a spectral field of only about $.0025\mu$, the use of Wien's equation is surely justified, and again the agreement was within 2° for the lower temperatures (see table). The sector method of calibrating is therefore justified and its advantages, involving as it does only one steady known temperature, are obvious.

3. A spectroscopic eye-piece for use with the Holborn-Kurlbaum pyrometer. The general form of the eye-piece is shown in Fig. 1; the spectroscopic instrument can be pointed and used just as the ordinary form, using a small auxiliary eye-piece and total reflecting prism which slides in a side tube just back of the lamp. The image of the comparison filament and of the hot surface are thrown in sharp focus across the middle of the spectroscope slit by an intermediate achromatic lens, the primary image of the hot surface having previously been brought into the plane of the comparison filament by focusing in the usual way, using the auxiliary eye-piece. The eye-piece and ocular slit of variable width are movable with a micrometer screw, giving about 500 divisions for the visible spectrum, and it is easy to work with an ocular slit covering not more than 25 A.E. The field then shows a central band due to the filament bordered by light from the hot surface. We have used the instrument very successfully to determine the absolute reflecting power of metallic surfaces. With a few properly chosen sectors, and an intense steady

source of light such as a Nernst glower reflecting powers can be measured to .2 per cent.[1]

The most interesting use of the instrument, however, is to test the validity of the use of Wien's logarithmic isochromatic equation for extending the range of the pyrometer scale, or for calibrating as above described. As pyrometers of the ordinary Holborn type are practically always used with Jena no. 2,745 red glass in the eye-piece to render the transmitted light approximately monochromatic, a comparison through a wide range of temperatures between the readings of the ordinary type (assuming the use of Wien's law to be allowable) and of the spectroscopic type (for which the use of Wien's law is hardly open to question) is of general interest. Our results are given in the table.[2] In computing these results the wave length of effective transmission of the red glass was taken as $\lambda = .658\ \mu$, as determined from spectrophotometric observations. Both instruments were calibrated by the sector method above described using the melting point of palladium as the standard temperature, 1549° C. Within the limits of accuracy which it is ordinarily possible to attain in optical pyrometry the use of Wien's equation in calibration or in extending the scale would therefore seem to be entirely justified.

TABLE.

Temperature, °C. as Determined by:	
"Red Glass" Pyrometer.	Spectroscopic Pyrometer.
1063	1062
1217	1218
1386	1387
1858	1861
1990	1990
2000	1995
2078	2080
2172	2174
2370	2380
2490	2500

SUMMARY.

This paper describes a convenient mounting, method of calibrating and spectroscopic eye-piece for the Holborn optical pyrometer, and gives a comparison of the "spectroscopic" and "red glass" temperature scale which justifies the use of Wien's Law with the ordinary "red glass" form of pyrometer.

UNIVERSITY OF WISCONSIN,
DEPARTMENT OF PHYSICS,
March, 1911.

[1] Since this instrument was constructed Henning (Zeit. f. Instk., March, 1910) has published a full account of a similar instrument which he also used for measuring reflecting power; this renders a detailed description unnecessary, though it should be mentioned that our form is much simpler than Henning's and can be used and sighted like an ordinary pyrometer.

[2] Observations taken by Mr. Forsythe and Mr. McCauley.

TEMPERATURE COEFFICIENTS OF ELECTRICAL RESISTANCE. III.

By A. A. Somerville.

TWO previous articles[1] in the Physical Review have described the apparatus used and its operation and have shown the results obtained in the case of twenty-one materials, most of them being commonly found in a laboratory.

In brief, the apparatus consists of a resistance furnace to heat the specimen, a platinum thermometer in connection with a Callendar temperature recorder to record the temperature of the furnace, a dial bridge

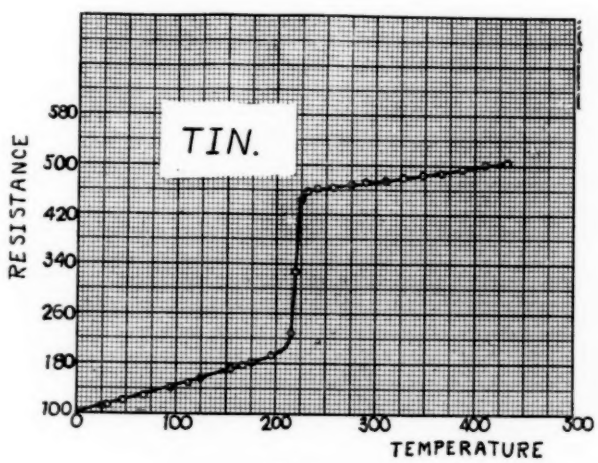

Fig. 1.

to measure the resistance of the specimen, a nitrogen producing plant made by air passing over hot copper and a pump to circulate the nitrogen over the specimen to prevent its oxidation while it is being heated and its resistance is being measured. In each case the material was heated to about 1050° C. unless it melted below that temperature.

During the past year, some of the materials that have been worked with are zinc, tin, german silver, brass, krupp, silicon, phosphor bronze, cupror, climax and monel metal.

[1] Phys. Rev., Vol. 30, No. 4, and Vol. 31, No. 3.

In the case of the pure metals, zinc and tin, having comparatively low melting points, the interesting feature is the change of resistance that takes place when the specimen passes from a solid to a liquid state and

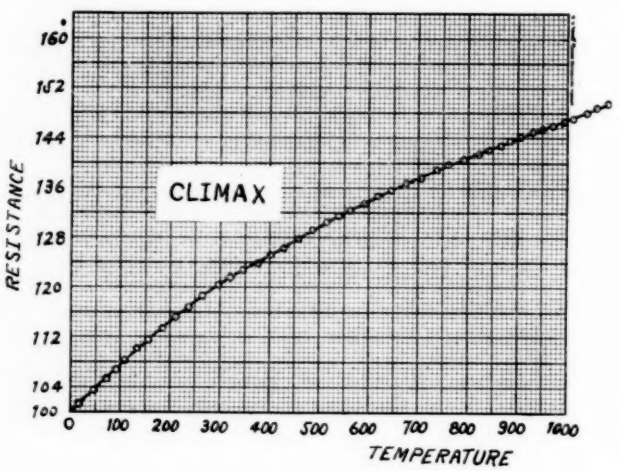

Fig. 2.

vice versa. Another interesting thing about zinc is that if it is drawn into a very fine wire and wrapped in the form of a spiral about a quartz tube the surface tension of the molten zinc is sufficient to hold it together for

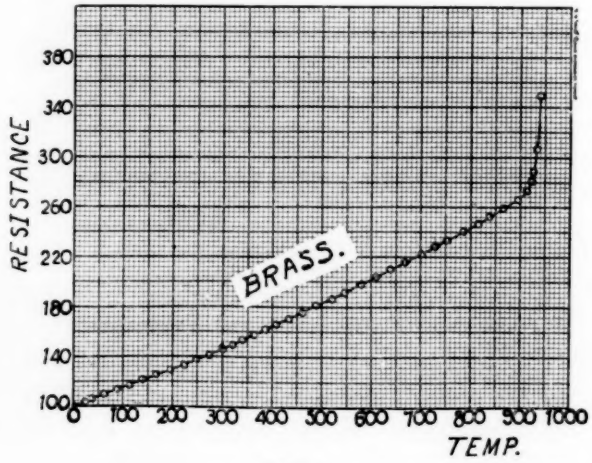

Fig. 3.

a considerable further increase in temperature and during this further heating the temperature coefficient of resistance is quite unusual, without doubt being negative and quite uniform for more than 100° before the

thread of zinc pulls apart. On the other hand, if the zinc is drawn into a small quartz tube as a containing vessel and its resistance measured there, the coefficient while in the molten state is almost zero.

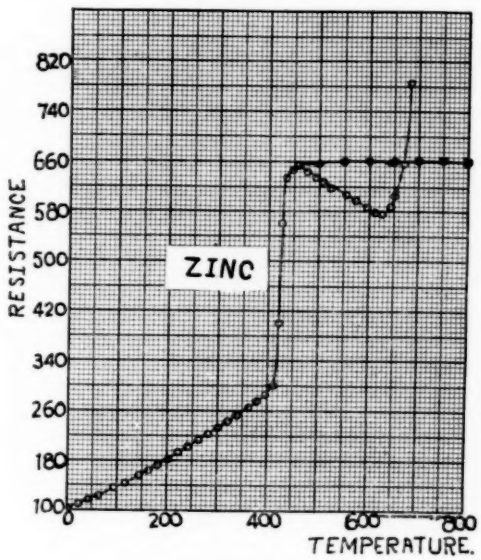

Fig. 4.

The silicon was in the form of rods a few centimeters in length and 2 or 3 mm. in diameter. Connections could be made only by looping

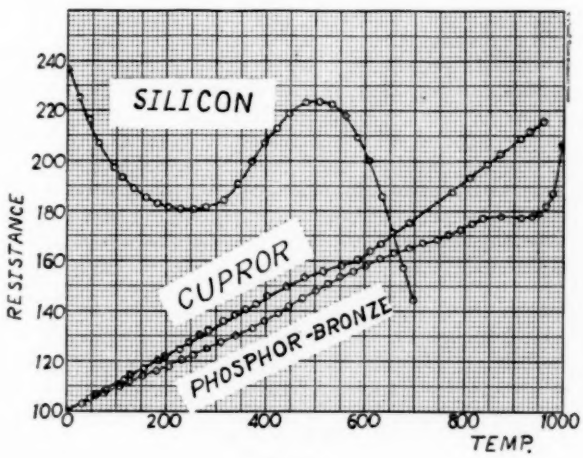

Fig. 5.

wires about a neck ground into either end of the silicon rod and drawing these wires taut by means of weights, so making mechanical rather than

electrical contact. Copper plating could not be made to hold lead wires on to the silicon, due to the different expansion of copper and silicon at higher temperatures. The curve shown was readily reproducible.

The other substances are alloys furnished by commercial firms which

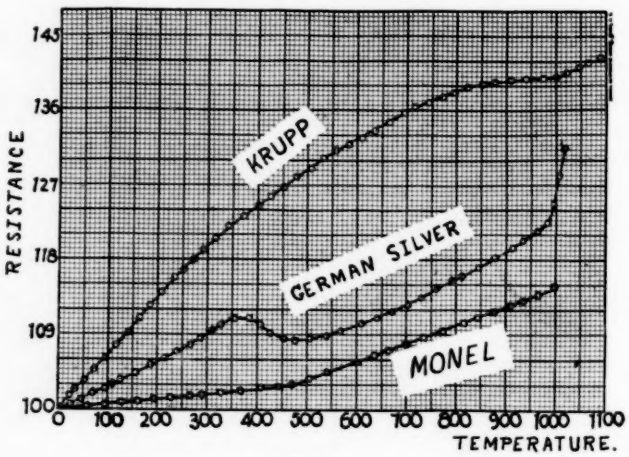

Fig. 6.

make claims for their usefulness for various purposes. They are all marked by comparatively low coefficients, as is characteristic of alloys in general, and most of them show marked changes in their coefficients, which is also generally to be expected in alloys.